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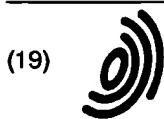
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(54) **Cyclopentadiene compound substituted with a hetero atom-containing group**

(57) Polysubstituted cyclopentadiene-containing compound, in which at least one substituent is of the form -RDR'_n, in which R is a linking group between the cyclopentadiene and the DR'_n group, D is a hetero atom selected from group 15 or 16 of the Periodic System of the Elements or an aryl group, in which case R has at least the length of an ethylene group, R' is a substituent and n is the number of R' groups bound to D.

Metal complexes in which at least one of these cyclopentadiene compounds is present as a ligand are useful as catalysts for the polymerisation of alpha-olefins.

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Description

The invention relates to a polysubstituted cyclopentadiene compound, of which at least one substituent is of the form $-RDR'_n$, in which R is a linking group between the cyclopentadiene and the group DR'_n , D is a hetero atom selected from group 15 or 16 of the Periodic System of the Elements, R' is a substituent and n is the number of R' groups bound to D.

Hereinafter, cyclopentadiene will be abbreviated to Cp. The same abbreviation will be used for a cyclopentadienyl group if it is clear, from the context, whether cyclopentadiene itself or its anion is meant.

In J. of Organomet. Chem., 479 (1994), 1-29 an overview is provided of the influence of the substituents on cyclopentadiene as a ligand in metal complexes. Here it is observed, on the one hand, that the chemical and physical properties of metal complexes can be varied over a wide range by adapting the substituents on the cyclopentadiene ring. On the other hand, it is stated that no predictions can be made concerning the effect to be expected of specific substituents. Another important statement in this publication is "An important feature of these catalyst systems is that tetravalent Ti centres are required for catalytic activity". Note should be taken, in this context, of the fact that Ti is exemplary for the metals which are suitable as a metal in the cyclopentadienyl-substituted metal complexes in question.

Surprisingly, it has now been found that excellent catalyst components having a high activity in the polymerization of α -olefins can be obtained if the Cp compounds according to the invention are used singly as a ligand on a metal which is not in its highest valency state. A mono-Cp-substituted metal complex of metals in a lower valency state than the highest possible is thus obtained, in which the Cp-containing ligand is multidentate-monoanionic and has a strongly stabilizing effect without at the same time blocking the active sites of the complex, so that the complexes have excellent catalytic activity.

A publication by Szymoniak et al. in J. Org. Chem. 1990, 55, 1429-1432 discloses a tetramethyl-substituted cyclopentadiene containing, as the fifth substituent, a diphenylphosphinyl group which is linked to the Cp either directly or via an ethylene group. The synthetic method described is highly specific, and nothing is taught as to whether, and if so how, Cp compounds substituted differently can be obtained. A publication by Jutzi et al. in Synthesis, 1993, 684 indicates that the above-described method of Szymoniak et al. mainly produces geminally substituted compounds, which cannot be used as anionic ligands in metal complexes. Geminally substituted Cp compounds are not suitable for use as a ligand and are not considered to be within the scope of the invention. DE-A-43.03.647 discloses Cp tetrasubstituted with methyl or ethyl groups and a group of the form RDR'_n , in which R is a methylene or ethylene group and D equals O, N or S.

A publication of Bensley et al. in J. Org. Chem., 1988, 53, 4417-4419 discloses a tetramethyl-substituted Cp containing, as the fifth substituent, a diphenylphosphinyl group which is coupled to the Cp via a propylene group.

A publication of Hafner et al. in Chemische Berichte, 1963, 661, 52-75 discloses a Cp substituted with 2 adjacent methyl groups in combination with a dimethylamino group which is coupled to the Cp via a methylene group.

EP-A-0.416.815 discloses a tetramethyl-substituted Cp containing, as the fifth substituent, an ethoxy group which is coupled to the Cp via a dimethylsilylene group.

Angew. Chem. Int. Ed. Engl. 1995, 34, pp. 2266-2267, discloses a Cp which is substituted with one tert-butyl group and to which, at the same time, a methoxy or an methoxy ethyl group is bound.

From none of the above-mentioned publications would those skilled in the art be able to deduce that the compounds according to the invention have a specific action as described above. Corresponding complexes in which the Cp compound is not substituted in the manner described prove unstable or, if they have been stabilized in some other way, are found to provide less active catalysts than the complexes containing substituted Cp compounds according to the invention, in particular in the case of the polymerization of α -olefins.

Moreover, the Cp compounds according to the invention are found to be able to stabilize highly reactive intermediates such as organometallic hydrides, organo borohydrides, organometallic alkyls and organometallic cations. Furthermore they prove suitable as stable and volatile precursors for use in metal chemical vapour deposition.

A polysubstituted Cp compound refers to a cyclopentadiene substituted with at least a group of the form RDR'_n and additionally with 1 to 4 R^2 groups to be defined hereinafter, H not being regarded as a substituent. Two of these R^2 groups may form a closed ring. Preferably, the polysubstituted Cp contains at least 2 R^2 groups as further substituents. Cp compounds thus substituted are found, when present as a ligand in a metal complex, to make said complex more suitable for the polymerization of α -olefins at a higher temperature than complexes substituted with other Cp compounds.

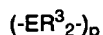
The Cp compound may also be a heterocyclopentadiene compound. Here and hereinafter the term heterocyclopentadiene group refers to a group which is derived from cyclopentadiene but in which at least one of the C atoms in the 5-ring thereof has been replaced by a hetero atom, which hetero atom can be selected from group 14, 15 or 16 of the Periodic System of the Elements. If more than one hetero atom is present in the 5-ring, these hetero atoms can be either identical or different. More preferably, the hetero atom is selected from group 15, and even more preferably the hetero atom is phosphorus.

The ring of the heterocyclopentadiene may carry, depending on the number of hetero atoms h, 1 till (4-h) substituents

R².

The R² groups may each, separately, be hydrogen or a hydrocarbon radical containing 1-20 carbon atoms (such as alkyl, aryl, aralkyl, and the like). Examples of such hydrocarbon radicals are methyl, ethyl, propyl, butyl, hexyl, decyl, phenyl, benzyl, and p-tolyl. Alternatively, two hydrocarbon radicals situated next to one another can be linked to one another in a ring system; R² may also be a substituent which in addition to, or instead of, carbon and/or hydrogen contains one or more hetero atoms from groups 14 and/or 17 of the Periodic System of the Elements, a hetero atom not being bound directly to the Cp. Thus a substituent may be a F-, or Si-containing group, R² may not contain a cyclopentadienyl group or a group derived therefrom.

The R group forms the link between the Cp and the DR'_n group. The length of the shortest link between the Cp and D, referred to below as the main chain of R, is critical insofar as it determines the accessibility of the metal by the DR'_n group in order thus to achieve the desired intramolecular coordination. Too small a length of the R group (or bridge) may mean that owing to ring strain the DR'_n group cannot coordinate effectively. R has a length of at least one atom. The R group can be a hydrocarbon group containing 1-20 carbon atoms (such as alkylidene, arylidene, arylalkylidene and the like). Examples of such groups are methylene, ethylene, propylene, butylene, phenylene, with or without a substituted side chain. Preferably, the R group has the following structure:



where p = 1-4 and E is an element from group 14 of the Periodic System. The R³ groups are as defined for R² plus hydrogen.

The main chain of the R group may consequently, in addition to carbon, also contain silicon or germanium. Examples of such R groups are: dialkylsilylene, dialkylgermylene, tetraalkyldisilylene or tetraalkylsilathylene (-SiR³₂CR³₂-). The alkyl groups in such a group preferably contain 1-4 C atoms and are, more preferably, a methyl or ethyl group.

The DR'_n group consists of a hetero atom D, selected from group 15 or 16 of the Periodic System of the Elements, and one or more substituent(s) R' bound to D. The number of R' groups (n) is linked to the type of the hetero atom D, in the sense that n = 2 if D is from group 15 and that n = 1 if D is from group 16. Preferably, the hetero atom D is selected from the group consisting of nitrogen (N), oxygen (O), phosphorus (P) or sulphur (S); more preferably, the hetero atom is nitrogen (N). The R' groups may be identical or different and may be chosen from the same groups as defined for R² with the exception of hydrogen. Preferably, the R' group is an alkyl, more preferably an n-alkyl group containing 1-20 C atoms. More preferably, the R' group is an n-alkyl containing 1-10 C atoms. Another possibility is for two R' groups in the DR'_n group to be joined together to give a ring. The DR'_n group can bind coordinatively to a metal.

If used as the only Cp-containing ligand in a metal complex in which the metal is not in the highest valency state, the polysubstituted Cp compounds are found to provide compounds having good stability and good catalytic activity. The invention therefore also relates to said use and the metal complexes obtained.

Metal complexes which are catalytically active if one of their ligands is a compound according to the invention are complexes of metals from groups 4-10 of the Periodic System of the Elements and rare earths (see the new IUPAC notation to be found on the inside of the cover of the Handbook of Chemistry and Physics, 70th Edition, 1989/1990). In this context, complexes of metals from groups 4 and 5 are preferably used as a catalyst component for polymerizing olefins, complexes of metals from groups 6 and 7 in addition also for metathesis and ring-opening metathesis polymerizations, and complexes of metals from groups 8-10 for olefin copolymerizations with polar comonomers, hydrogenations and carbonylations. Particularly suitable for the polymerization of polyolefins are such metal complexes in which the metal is chosen from the group consisting of Ti, Zr, Hf, V and Cr.

The term olefins here and hereinafter refers to α -olefins, diolefins and other ethylenically unsaturated monomers. If the term polymerization of olefins is used, this refers both to the polymerization of a single type of olefinic monomer and to the copolymerization of two or more olefins.

The invention therefore also relates to the metal complexes thus composed, in which the metal is not in the highest valency state, and to the use thereof as catalyst components, in particular for polymerization of olefins, linear as well as branched and cyclic olefins and dienes which may or may not be conjugated, and mixtures thereof. Preferably the metal is chosen from the group consisting of Ti(III), Zr(III), Hf(III) and V(IV).

The sequence in which the substituents are attached to the Cp depends on the type of the R² groups and the RDR'₂ group. Sometimes it is possible first to attach the substituents R² to the Cp and then the RDR'_n group, and sometimes the inverse order is observed. Cp compounds substituted with a number of R² groups may, for example, be prepared by reacting a halide of the substituting compound in a mixture of the Cp compound and an aqueous solution of a base in the presence of a phase transfer catalyst. It is possible to use virtually equivalent quantities of the halogenated substituting compounds with respect to the Cp compound. An equivalent quantity is understood as a quantity in moles which corresponds to the desired substitution multiplicity, for example 2 moles per mole of Cp compound if disubstitution with the substituent in question is intended.

Depending on the size and the associated steric hindrance of the compounds to be substituted it is possible to obtain at most trisubstituted to pentasubstituted Cp compounds. If a reaction with tertiary halides is carried out, as a

rule only trisubstituted Cp compounds can be obtained, whereas with primary and secondary halides it is generally possible to achieve tetra- and often even pentasubstitution.

Substituents which can be attached by means of this method are, for example, alkyl groups, both linear and branched, and cyclic, alkenyl and aralkyl groups. It is also possible for these to contain, in addition to carbon and hydrogen, one or more hetero atoms from groups 14-17 of the Periodic System of the Elements, for example, O, N, Si or F. Examples of suitable groups are methyl, ethyl, (iso)propyl, sec-butyl, -pentyl, -hexyl and -octyl, (tert-)butyl and higher homologues, cyclohexyl, benzyl.

The substituents are preferably used in the method in the form of their halides and more preferably in the form of their bromides. If bromides are used a smaller quantity of phase transfer catalyst is found to be sufficient, and a higher yield of the compound aimed for is found to be achieved.

By means of this method it is also possible, without intermediate isolation or purification, to obtain Cp compounds which are substituted specific combinations of substituents. Thus, for example, disubstitution with the aid of a certain halide can first be carried out and in the same reaction mixture a third substitution with a different substituent, by a second, different halide being added to the mixture after a certain time. This can be repeated, so that it is also possible to prepare Cp derivatives having three or more different substituents.

The substitution takes place in a mixture of the Cp compound and an aqueous solution of a base. The concentration of the base in the solution is in the range between 20 and 80 wt.%. Hydroxides of an alkali metal, for example K or Na, are highly suitable as a base. The base is present in an amount of 5-30 moles, preferably 6-20 moles, per mole of Cp compound. It was found that the reaction time can be considerably shortened if the solution of the base is refreshed during the reaction, for example by first mixing the solution with the other components of the reaction mixture and after some time isolating the aqueous phase and replacing it by a fresh quantity of the solution of the base.

The substitution takes place at atmospheric or elevated pressure, for example up to 100 Mpa, the latter particularly when volatile components are present. The temperature at which the reaction takes place can vary between wide limits, for example from -20 to 120°C, preferably between 10 and 50°C. Initiating the reaction at room temperature is suitable, as a rule, whereupon the temperature of the reaction mixture may rise as a result of the heat liberated in the course of the reaction.

The substitution takes place in the presence of a phase transfer catalyst which is able to transfer OH ions from the aqueous phase to the organic phase containing Cp and the substituting compound. The OH ions react in the organic phase with an H atom which can be split off from the Cp compound. Possible phase transfer catalysts to be used are quaternary ammonium, phosphonium, arsonium, stibonium, bismuthonium, and tertiary sulphonium salts. More preferably, ammonium and phosphonium salts are used, for example tricaprylmethylammonium chloride, commercially available under the name Aliquat 336 (Fluka AG, Switzerland; General Mills Co., USA) and Adogen 464 (Aldrich Chemical Co., USA). Compounds such as benzyltriethylammonium chloride (TEBA) or benzyltriethylammonium bromide (TEBA-Br), benzyltrimethylammonium chloride, benzyltrimethylammonium bromide or benzyltrimethylammonium hydroxide (Triton B), tetra-n-butylammonium chloride, tetra-n-butylammonium bromide, tetra-n-butylammonium iodide, tetra-n-butylammonium hydrogen sulphate or tetra-n-butylammonium hydroxide and cetyltrimethylammonium bromide or cetyltrimethylammonium chloride, benzyltributyl-, tetra-n-pentyl-, tetra-n-hexyl- and trioctylpropylammonium chlorides and their bromides are likewise suitable. Usable phosphonium salts include, for example, tributylhexadecylphosphonium bromide, ethyltriphenylphosphonium bromide, tetraphenylphosphonium chloride, benzyltriphenylphosphonium iodide and tetrabutylphosphonium chloride. Crown ethers and cryptands can also be used as a phase transfer catalyst, for example 15-crown-5, 18-crown-6, dibenzo-18-crown-6, dicyclohexano-18-crown-6, 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane (Kryptofix 221), 4,7,13,18-tetraoxa-1,10-diazabicyclo[8.5.5]eicosane (Kryptofix 211) and 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane ("[2.2.2]") and its benzo derivative Kryptofix 222 B. Polyethers such as ethers of ethylene glycols can also be used as a phase transfer catalyst. Quaternary ammonium salts, phosphonium salts, phosphoric acid triamides, crown ethers, polyethers and cryptands can also be used on supports such as, for example, on a crosslinked polystyrene or another polymer. The phase transfer catalysts are used in an amount of 0.01-2, preferably 0.05-1, equivalents on the basis of the amount of Cp compound.

In carrying out the process the components can be added to the reactor in various sequential orders.

After the reaction is complete, the aqueous phase and the organic phase which contains the Cp compound are separated. When necessary, the Cp compound is recovered by fractionated distillation.

An alternative method of preparation for alkyl-substituted cyclopentadienes is that via alkyl-substituted acetylenes with the aid of a titanium catalyst, disclosed by C.M. Garner, Tet. Lett., vol. 35, 1994, p.2463. Tetraalkyl-substituted cyclopentadienes can also be synthesized by reaction of 2-lithium-2-alkenes with an ester, followed by a ring closure to give the cyclopentadiene derivative, as described in D.M. Bensley, J. Org. Chem., 53, (1988), 4417. According to the above-described synthesis methods, however, only tetraalkylcyclopentadienes having 4 identical alkyl groups can be prepared.

From acetylenes it is also possible to prepare, with the aid of tetracarbonyl nickel, cyclopentenone derivatives. Reaction of the cyclopentenone obtained with a metal alkyl reagent (for example an alkyllithium or a Grignard reagent), followed by abstraction of water results in a corresponding cyclopentadiene derivative. Via this route, however, only

cyclopentadiene derivatives having 4 identical substituents can be synthesized, as described in B. Fell, Chem. Ber. 109, (1976), 2914. Cyclopentenones containing different alkyl substituents can be synthesized by the Nazarov reaction, from α - β -unsaturated esters. The cyclopentenones obtained can, as described above, be converted into cyclopentadienes. This reaction is disclosed by J.-M. Conia, Bul. Soc. Chim. France, 8-9, (1970), 2992. Cyclopentadiene derivatives can be converted into fulvenes, which can react with metal alkyl reagents to give more highly substituted cyclopentadiene derivatives (for this see Stone K.J., J. Org. Chem., (49) 1984, 1849).

The group of the form RDR'_n is attached at a free position of the Cp compound previously substituted at one or more positions, for example according to the following synthetic route.

During a first step of this route a substituted Cp compound is deprotonated by reaction with a base, sodium or potassium.

Possible bases to be used are, for example, organolithium compounds (R^3Li) or organomagnesium compounds (R^3MgX), where R^3 is an alkyl, aryl or aralkyl group, and X is a halide, for example n-butyllithium or i-propylmagnesium chloride. Potassium hydride, sodium hydride, inorganic bases, for example NaOH and KOH, and alcoholates and amides of Li, K and Na can likewise be used as a base. Mixtures of the abovementioned compounds can also be used.

This reaction can be carried out in a polar dispersant, for example an ether. Examples of suitable ethers are tetrahydrofuran (THF) or dibutyl ether. Apolar solvents such as, for example, toluene, can likewise be employed.

Subsequently, during a second step of the synthesis route, the cyclopentadienyl anion formed reacts with a compound according to the formula (R'_nD-R-Y) , $(X-R-Y)$ or $(X-R-Sul)$, in which D, R, R' and n are as defined hereinabove. Y is a halogen atom (X) or a sulphonyl group (Sul). Examples of halogen atoms X are chlorine, bromine and iodine. Preferably, the halogen atom X is a chlorine atom or bromine atom. The sulphonyl group takes the form $-OSO_2R^6$, in which R^6 is a hydrocarbon radical containing 1-20 carbon atoms, for example alkyl, aryl, aralkyl. Examples of such hydrocarbon radicals are butane, pentane, hexane, benzene, naphthalene. Instead of, or in addition to, carbon and/or hydrogen, R^6 may also contain one or more hetero atoms from groups 14-17 of the Periodic System of the Elements, such as N, O, Si or F. Examples of sulphonyl groups are: phenylmethanesulphonyl, benzenesulphonyl, 1-butan-1-ylsulphonyl, 2,5-dichlorobenzenesulphonyl, 5-dimethylamino-1-naphthalenesulphonyl, pentafluorobenzenesulphonyl, p-toluenesulphonyl, trichloromethanesulphonyl, trifluoromethanesulphonyl, 2,4,6-triisopropylbenzenesulphonyl, 2,4,6-trimethylbenzenesulphonyl, 2-mesitylenesulphonyl, methanesulphonyl, 4-methoxybenzenesulphonyl, 1-naphthalenesulphonyl, 2-naphthalenesulphonyl, ethanesulphonyl, 4-fluorobenzenesulphonyl and 1-hexadecanesulphonyl. Preferably, the sulphonyl group is p-toluenesulphonyl or trifluoromethanesulphonyl.

If D is a nitrogen atom and Y is a sulphonyl group, the compound according to the formula (R'_nD-R-Y) is formed in situ by reaction of an aminoalcohol compound (R'_2NR-OH) with a base (such as defined hereinabove), potassium or sodium, followed by a reaction with a sulphonyl halide (Sul-X).

The second reaction step can likewise be carried out in a polar dispersant such as described for the first step. The temperature at which the reactions are carried out is between -60 and 80°C. Reactions with $X-R-Sul$, $X-R-Y$ and with R'_nD-R-Y , in which Y is Br or I, are as a rule carried out at a temperature between -20 and 20°C. Reactions with R'_nD-R-Y , in which Y is Cl, are as a rule carried out at a higher temperature (10 to 80°C). The upper limit for the temperature at which the reactions are carried out is determined, inter alia, by the boiling point of the compound R'_nD-R-Y and that of the solvent used.

After the reaction with a compound according to the formula $(X-R-Sul)$ or $(X-R-Y)$ a further reaction is carried out with $LiDR'_n$ or HDR'_n to replace X by a DR'_n functionality. To this end a reaction is carried out, optionally in the same dispersant as mentioned above, at 20 to 80°C.

In the course of this synthesis process it is possible, when substituted Cp compounds are being alkylated, for geminal products to be formed in part. A geminal substitution is a substitution in which the number of substituents increases by 1 but in which the number of substituted carbon atoms does not increase. The amount of geminal products formed is low if the synthesis is carried out starting from a substituted Cp compound having 1 substituent and increases the more substituents the substituted Cp compound contains. In the presence of sterically large substituents in the substituted Cp compound no or virtually no geminal products are formed. Examples of sterically large substituents are secondary or tertiary alkyl substituents.

The amount of geminal product formed is also low if the second step of the reaction is carried out under the influence of a Lewis base whose conjugated acid has a dissociation constant with a pK_a of less than or equal to -2.5. The pK_a values are based on D.D. Perrin: Dissociation Constants of Organic Bases in Aqueous Solution, International Union of Pure and Applied Chemistry, Butterworths, London 1965. The values have been determined in aqueous H_2SO_4 solution. Ethers may be mentioned as an example of suitable weak Lewis bases.

If geminal products have been formed during the process according to the invention, these products can be separated in a simple manner from the non-geminal products by converting the mixture of geminal and non-geminal substituted products into a salt, by reaction with potassium, sodium or a base, the salt then being washed with a dispersant in which the salt of the non-geminal products is insoluble or sparingly soluble. Bases which can be used include the compounds as mentioned above. Suitable dispersants are apolar dispersants such as alkanes. Examples of suitable alkanes are heptane and hexane.

Other bridge systems can be synthesized from (cyclopentadienyl)dialkylsilyl halides. Reaction of the silyl halide with a nucleophile, for example lithiumdialkylamides, -phosphides or -arsides results in a silyl-bridged system with a donor hetero atom. In an identical manner it is possible to synthesize di-sila-bridged systems.

From fulvenes it is possible to synthesize bridged systems containing a donor hetero atom and one carbon atom in the bridge, as described in D.M. Bensley, J. Org. Chem., 53, (1988), 4417.

The synthesis of metal complexes containing the above-described specific Cp compounds as a ligand may take place according to the processes known per se for this purpose. The use of these Cp compounds does not require any adaptations of said known processes.

Metal complexes supported on a carrier can also be used.

The polymerization of α -olefins, for example ethylene, propylene, butene, hexene, octene and mixtures thereof and combinations with dienes can be carried out in the presence of the metal complexes containing the cyclopentadienyl compounds according to the invention as a ligand. Particularly suitable for this purpose are the complexes of transition metals, not in their highest valency state, in which just one of the cyclopentadienyl compounds according to the invention is present as a ligand, and in which the metal is cationic during the polymerization. These polymerizations can be carried out in the manner known for this purpose, and the use of the metal complexes as a catalyst component does not require any significant adaptation of these processes. The known polymerizations are carried out in suspension, solution, emulsion, gas phase or as a bulk polymerization. It is customary to use, as a cocatalyst, an organometallic compound, the metal being selected from group 1, 2, 12 or 13 of the Periodic System of the Elements. Examples include trialkylaluminum, alkylaluminum halides, alkylaluminumoxanes (such as methylaluminumoxanes), tris(pentafluorophenyl) borane, dimethylanilinium tetra(pentafluorophenyl) borate or mixtures thereof. The polymerizations are carried out at temperatures between -50°C and $+350^{\circ}\text{C}$, more in particular between 25 and 250°C . Pressures used are generally between atmospheric pressure and 250 MPa, for bulk polymerizations more in particular between 50 and 250 MPa, for the remaining polymerization processes between 0.5 and 25 MPa. As dispersants and solvents use can be made, for example, of hydrocarbons such as pentane, heptane and mixtures thereof. Aromatic, optionally perfluorinated hydrocarbons likewise deserve consideration. The monomer to be employed in the polymerization can also be used as a dispersant or solvent.

The invention will be explained with reference to the following examples, but is not limited thereto. Characterization of the products obtained involved the following analytical methods.

Gas chromatography (GC) was carried out on a Hewlett-Packard 5890 series II with an HP crosslinked methyl silicon gum (25 m \times 0.32 mm \times 1.05 μm) column. Combined gas chromatography/ mass spectrometry (GC-MS) was carried out with a Fisons MD800 equipped with a quadrupole mass detector, autoinjector Fisons AS800 and CPSil8 column (30 m \times 0.25 mm \times 1 μm , low bleed). NMR was carried out on a Bruker ACP200 (^1H =200 MHz; ^{13}C =50 MHz) or Bruker ARX400 (^1H =400 MHz; ^{13}C =100 MHz). To characterize metal complexes of a Kratos MS80 or alternatively a Finnigan Mat 4610 mass spectrometer was used.

Example I

Preparation of di(2-propyl)cyclopentadiene

In a double-walled reactor having a volume of 200 mL, provided with baffles, condenser, top stirrer, thermometer and dropping funnel, 180 g of clear 50% strength NaOH (2.25 mol), 9.5 g of Aliquat 336 (23 mmol) and 15 g (0.227 mol) of freshly cracked cyclopentadiene were combined. The reaction mixture was stirred turbulently at a speed of 1385 rpm for a few minutes. Then 56 g of 2-propyl bromide (0.46 mol) were added, cooling with water taking place at the same time. A few minutes after the addition of the 2-propyl bromide the temperature rose by approximately 10°C . Stirring then continued for 6 hours at 50°C . GC was used to show that at that instant 92% of di(2-propyl)cyclopentadiene was present in the mixture of di- and tri(2-propyl)cyclopentadiene. The product was distilled at 10 mbar and 70°C . After distillation, 25.35 g of di(2-propyl)cyclopentadiene were obtained. Characterization took place with the aid of GC, GC-MS, ^{13}C - and ^1H -NMR.

Example II

Preparation of tri(2-propyl)cyclopentadiene

In a double-walled reactor having a volume of 200 mL, provided with baffles, condenser, top stirrer, thermometer and dropping funnel, 180 g of clear 50% strength NaOH (2.25 mol), 9.5 g of Aliquat 336 (23 mmol) and 15 g (0.227 mol) of freshly cracked cyclopentadiene were combined. The reaction mixture was stirred turbulently at a speed of 1385 rpm for a few minutes. Then 84 g of 2-propyl bromide (0.68 mol) were added, cooling with water taking place at the same time. A few minutes after the addition of the 2-propyl bromide the temperature rose by approximately 10°C . GC was used to show that approximately 30 minutes after the addition of all the 2-propyl bromide (monosubstituted) 2-propylcy-

clopentiadiene had been formed. The reaction mixture was then heated to 50°C. After 2 hours, stirring was stopped and phase separation was awaited. The water layer was drawn off, and 180 g (2.25 mol) of fresh 50% strength NaOH were added. Stirring then continued for one hour at 50°C. GC was used to show that at that instant between 90 and 95% of tri(2-propyl)cyclopentadiene was present in the mixture of di-, tri- and tetra-(2-propyl)cyclopentadiene. The product was distilled at 1.3 mbar and 77-78°C. After distillation, 31.9 g of tri(2-propyl)cyclopentadiene were obtained. Characterization took place with the aid of GC, GC-MS, ¹³C- and ¹H-NMR.

Example III

Preparation of tetra(2-propyl)cyclopentadiene

Analogous to Example II, but now 114 g of 2-propyl bromide (0.93 mol) were added, and after 7 hours the water layer was replaced a second time. At the same time, a further 5 g (12 mmol) of Aliquat 336 were added. Heating then took place for 16 hours at 55°C. GC was used to show that at that instant 85% of tetra(2-propyl)cyclopentadiene was present in the mixture of tri- and tetra(2-propyl)cyclopentadiene. The product was distilled at 1.0 mbar and 88-90°C. After distillation, 34.9 g of tetra(2-propyl)cyclopentadiene were obtained. Characterization took place with the aid of GC, GC-MS, ¹³C- and ¹H-NMR.

Example IV

Preparation of di(cyclohexyl)cyclopentadiene

A double-walled reactor having a volume of 1 L, provided with baffles, condenser, top stirrer, thermometer and dropping funnel, was charged with 600 g of clear 50% strength NaOH (7.5 mol), followed by cooling to 8°C. Then 20 g of Aliquat 336 (49 mmol) and 33 g (0.5 mol) of freshly cracked cyclopentadiene were added. The reaction mixture was stirred turbulently for a few minutes. Then 172 g of cyclohexyl bromide (1.05 mol) were added, cooling with water taking place at the same time. After 2 hours' stirring at room temperature the reaction mixture was heated to 70°C, followed by a further 6 hours' stirring. GC was used to show that at that instant 79% of di(cyclohexyl)cyclopentadiene was present. The product was distilled at 0.04 mbar and 110-120°C. After distillation, 73.6 g of di(cyclohexyl)cyclopentadiene were obtained. Characterization took place with the aid of GC, GC-MS, ¹³C- and ¹H-NMR.

Example V

Preparation of di- and tri(3-pentyl)cyclopentadiene

A double-walled reactor having a volume of 1 L, provided with baffles, condenser, top stirrer, thermometer and dropping funnel, was charged with 430 g (5.4 mol) of clear 50% strength NaOH. Then 23 g of Aliquat 336 (57 mmol) and 27 g (0.41 mol) of freshly cracked cyclopentadiene were added. The reaction mixture was stirred turbulently for a few minutes. Then 150 g of 3-pentyl bromide (1.0 mol) were added over a period of 1 hour, cooling with water taking place at the same time. After 1 hour's stirring at room temperature the reaction mixture was heated to 70°C, followed by a further 3 hours' stirring. Stirring was stopped and phase separation was awaited. The water layer was drawn off and 540 g (6.70 mol) of fresh 50% strength NaOH were added, followed by a further 4 hours' stirring at 70°C. GC was used to show that at that instant the mixture consisted of di- and tri(3-pentyl)cyclopentadiene (approximately 3 : 2). The products were distilled at 0.2 mbar, 51°C and 0.2 mbar, 77-80°C, respectively. After distillation, 32 g of di- and 18 g of tri(3-pentyl)cyclopentadiene were obtained. Characterization took place with the aid of GC, GC-MS, ¹³C- and ¹H-NMR.

Example VI

Preparation of tri(cyclohexyl)cyclopentadiene

A double-walled reactor having a volume of 1 L, provided with baffles, condenser, top stirrer, thermometer and dropping funnel, was charged with 600 g of clear 50% strength NaOH (7.5 mol), followed by cooling to 8°C. Then 20 g of Aliquat 336 (49 mmol) and 33 g (0.5 mol) of freshly cracked cyclopentadiene were added. The reaction mixture was stirred turbulently for a few minutes. Then 256 g of cyclohexyl bromide (1.57 mol) were added, cooling with water taking place at the same time. After 1 hour's stirring at room temperature the reaction mixture was heated to 70°C, followed by a further 2 hours' stirring. After 2 hours, stirring was stopped and phase separation was awaited. The water layer was drawn off and 600 g (7.5 mol) of fresh 50% strength NaOH were added, followed by a further 4 hours' stirring at 70°C. GC was used to show that at that instant 10% of di- and 90% of tri(cyclohexyl)cyclopentadiene were present in the mixture. The product was distilled at 0.04 mbar and 130°C. After distillation, 87.4 g of tri(cyclohexyl)cyclopentadiene were

obtained. Characterization took place with the aid of GC, GC-MS, ^{13}C - and ^1H -NMR.

Example VII

Preparation of di(2-butyl)cyclopentadiene

A double-walled reactor having a volume of 1 L, provided with baffles, condenser, top stirrer, thermometer and dropping funnel, was charged with 600 g of clear 50% strength NaOH (7.5 mol), followed by cooling to 10°C. Then 30 g of Aliquat 336 (74 mmol) and 48.2 g (0.73 mol) of freshly cracked cyclopentadiene were added. The reaction mixture was stirred turbulently for a few minutes. Then 200 g of 2-butyl bromide (1.46 mol) were added over a period of half an hour, cooling with water taking place at the same time. After 2 hours' stirring at room temperature the reaction mixture was heated to 60°C, followed by a further 4 hours' stirring. GC was used to show that at that instant more than 90% of di(2-butyl)cyclopentadiene was present in the mixture. The product was distilled at 20 mbar and 80-90°C. After distillation, 90.8 g of di(2-butyl)cyclopentadiene were obtained. Characterization took place with the aid of GC, GC-MS, ^{13}C - and ^1H -NMR.

Example VIII

Preparation of tri(2-butyl)cyclopentadiene

A double-walled reactor having a volume of 1 L, provided with baffles, condenser, top stirrer, thermometer and dropping funnel, was charged with 400 g of clear 50% strength NaOH (5 mol). Then 9.6 g of Aliquat 336 (24 mmol) and 15.2 g (0.23 mol) of freshly cracked cyclopentadiene were added. The reaction mixture was stirred turbulently for a few minutes. Then 99.8 g of 2-butyl bromide (0.73 mol) were added over a period of half an hour, cooling with water taking place at the same time. After half an hour's stirring at room temperature the reaction mixture was heated to 70°C, followed by a further three hours' stirring. Stirring was stopped and phase separation was awaited. The water layer was drawn off and 400 g (5.0 mol) of fresh 50% strength NaOH were added, followed by a further two hours' stirring at 70°C. GC was used to show that at that instant more than 90% of tri(2-butyl)cyclopentadiene was present in the mixture of di-, tri- and tetra(2-butyl)cyclopentadiene. The product was distilled at 1 mbar and 91°C. After distillation, 40.9 g of tri(2-butyl)cyclopentadiene were obtained. Characterization took place with the aid of GC, GC-MS, ^{13}C - and ^1H -NMR.

Example IX

Preparation of di- and tri(2-pentyl)cyclopentadiene

A double-walled reactor having a volume of 1 L, provided with baffles, condenser, top stirrer, thermometer and dropping funnel, was charged with 900 g (11.25 mol) of clear 50% strength NaOH. Then 31 g of Aliquat 336 (77 mmol) and 26.8 g (0.41 mol) of freshly cracked cyclopentadiene were added. The reaction mixture was stirred turbulently for a few minutes. Then 155 g of 2-pentyl bromide (1.03 mol) were added over a period of 1 hour, cooling with water taking place at the same time. After 3 hours' stirring at room temperature the reaction mixture was heated to 70°C, followed by a further 2 hours' stirring. Stirring was stopped and phase separation was awaited. The water layer was drawn off and 900 g (11.25 mol) of fresh 50% strength NaOH were added, followed by a further two hours' stirring at 70°C. GC was used to show that at that instant the mixture consisted of di- and tri(2-pentyl)cyclopentadiene (approximately 1 : 1). The products were distilled at 2 mbar, 79-81°C and 0.5 mbar, 102°C, respectively. After distillation, 28 g of di- and 40 g of tri(2-pentyl)cyclopentadiene were obtained. Characterization took place with the aid of GC, GC-MS, ^{13}C - and ^1H -NMR.

Example X

Preparation of di(2-propyl)cyclohexylcyclopentadiene

In a double-walled reactor having a volume of 200 mL, provided with baffles, condenser, top stirrer, thermometer and dropping funnel, 150 g of clear 50% strength NaOH (1.9 mol), 7 g of Aliquat 336 (17.3 mmol) and 8.5 g (0.13 mol) of freshly cracked cyclopentadiene were combined. The reaction mixture was stirred turbulently at a speed of 1385 rpm for a few minutes. Then 31.5 g of 2-propyl bromide (0.26 mol) were added, cooling with water taking place at the same time. Metering in took a total time of 1 hour. After addition of the bromide the reaction mixture was heated to 50°C. After 2 hours, stirring was stopped and phase separation was awaited. The water layer was drawn off, and 150 g (1.9 mol) of fresh 50% strength NaOH were added. This was followed by the addition of 20.9 g (0.13 mol) of cyclohexyl bromide, and stirring then continued for a further 3 hours at 70°C. GC was used to show that at that instant 80% of di(2-pro-

pyl)cyclohexylcyclopentadiene was present in the mixture. The product was distilled at 0.3 mbar and 80°C. After distillation, 17.8 g of di(2-propyl)cyclohexylcyclopentadiene were obtained. Characterization took place with the aid of GC, GC-MS, ^{13}C - and ^1H -NMR.

5 Example XI

Preparation of tetra(octyl)cyclopentadiene

A double-walled reactor having a volume of 1.5 L, provided with baffles, condenser, top stirrer, thermometer and dropping funnel, was charged with 900 g of clear 50% strength NaOH (11.3 mol), followed by cooling to 10°C. Then 30 g of Aliquat 336 (74 mmol) and 48 g (0.72 mol) of freshly cracked cyclopentadiene were added. The reaction mixture was stirred turbulently for a few minutes. Then 577 g of octyl bromide (2.99 mol) were added over a period of one hour, cooling with water taking place at the same time. After 1 hour's stirring at room temperature the reaction mixture was heated to 35°C, followed by a further 6 hours' stirring. Stirring was stopped and phase separation was awaited. The water layer was drawn off and 920 g (11.5 mol) of fresh 50% strength NaOH were added, followed by a further 5 hours' stirring at room temperature. GC was used to show that at that instant 10% of tri-, 83% of tetra- and 7% of penta (octyl)cyclopentadiene were present in the mixture. The product was distilled under reduced pressure. After vacuum distillation, 226.6 g of tetra(octyl)cyclopentadiene were obtained. The product was characterized with the aid of GC, GC-MS, ^{13}C - and ^1H -NMR.

20 Example XII

Preparation of tetra(n-propyl)cyclopentadiene

A double-walled reactor having a volume of 1 L, provided with baffles, condenser, top stirrer, thermometer and dropping funnel, was charged with 1000 g of clear 50% strength NaOH (12.5 mol), followed by cooling to 10°C. Then 30 g of Aliquat 336 (74 mmol) and 50 g (0.75 mol) of freshly cracked cyclopentadiene were added. The reaction mixture was stirred turbulently for a few minutes. Then 373 g of propyl bromide (3.03 mol) were added over a period of one hour, cooling with water taking place at the same time. After 1 hour's stirring at room temperature the reaction mixture was heated to 35°C, followed by a further 6 hours' stirring. Stirring was stopped and phase separation was awaited. The water layer was drawn off and 990 g (12.4 mol) of fresh 50% strength NaOH were added, followed by a further 5 hours' stirring at room temperature. GC was used to show that at that instant 14% of tri-, 80% of tetra- and 6% of penta (propyl)cyclopentadiene were present in the mixture. The product was distilled under reduced pressure. After vacuum distillation, 103.1 g of tetra(propyl)cyclopentadiene were obtained. The product was characterized with the aid of GC, GC-MS, ^{13}C - and ^1H -NMR.

Example XIII

Preparation of di(2-phenyl-propyl)cyclopentadiene

A double-walled reactor having a volume of 1 L, provided with baffles, condenser, top stirrer, thermometer and dropping funnel, was charged with 600 g of clear 50% strength NaOH (7.5 mol), followed by cooling to 8°C. Then 20 g of Aliquat 336 (49 mmol) and 33 g (0.5 mol) of freshly cracked cyclopentadiene were added. The reaction mixture was stirred turbulently for a few minutes. Then 219 g of 1-bromo-2-phenylpropane (1.1 mol) were added, all at once, cooling with water taking place at the same time. After 2 hours' stirring at room temperature the reaction mixture was heated to 70°C, followed by a further 6 hours' stirring. GC was used to show that at that instant 89% of di(2-phenyl-propyl)cyclopentadiene was present. The product was distilled at low pressure and high temperature, whereupon 95.34 g (0.4 mol; 80%) of di(2-phenyl-propyl)cyclopentadiene were obtained. The product was characterized with the aid of GC, GC-MS, ^{13}C - and ^1H -NMR.

50 Example XIV

Preparation of di(1,1-dimethylpropyl)cyclopentadiene

A double-walled reactor having a volume of 1 L, provided with baffles, condenser, top stirrer, thermometer and dropping funnel, was charged with 600 g of clear 50% strength NaOH (7.5 mol), followed by cooling to 8°C. Then 20 g of Aliquat 336 (49 mmol) and 33 g (0.5 mol) of freshly cracked cyclopentadiene were added. The reaction mixture was stirred turbulently for a few minutes. Then 226.6 g of 2-bromo-2-methylbutane (1.5 mol) were added, all at once, cooling with water taking place at the same time. After 2 hours' stirring at room temperature the reaction mixture was heated to

70°C, followed by a further 6 hours' stirring. GC was used to show that at that instant 56% of di(1,1-dimethyl-propyl)cyclopentadiene was present. The product was distilled at low pressure and high temperature, whereupon 47.7 g (0.23 mol; 46%) of di(1,1-dimethyl-propyl)cyclopentadiene were obtained. The product was characterized with the aid of GC, GC-MS, ^{13}C - and ^1H -NMR.

Example XV

Preparation of di(1-methyl-1-ethyl-propyl)cyclopentadiene

This preparation was carried out as in the preceding example, but now with: 247.6 grams of 3-bromo-3-methylpentane. In the first instance 55%, and after distillation 43% (50.4 grams) of di(1-methyl-1-ethyl-propyl)cyclopentadiene were obtained.

Experiment XVI

In-situ preparation of 2-(N,N-dimethylaminoethyl) tosylate

Under dry nitrogen, a solution of n-butyllithium in hexane (1 equivalent) in dry THF was added (metering time: 60 minutes) at -10°C to a solution of 2-dimethyl-aminoethanol (1 equivalent) in a three-necked round-bottomed flask provided with a magnetic stirrer and a dropping funnel. After the addition of all the butyllithium the mixture was brought to room temperature and stirred for 2 hours. Subsequently the mixture was cooled (-10°C) and p-toluenesulphonyl chloride (1 equivalent) was then added, followed by 15 minutes' stirring at this temperature, before the solution was added to a cyclopentadienyl anion.

By a similar method, comparable tosylates can be prepared. In a number of the following examples a tosylate is in each case coupled with alkylated Cp compounds. In the course of said coupling the required substitution reaction is accompanied by geminal coupling. In almost all cases it was possible to separate the geminal isomers from the non-geminal isomers by conversion of the non-geminal isomers into their sparingly soluble potassium salt, followed by this salt being washed with a solvent in which said salt is insoluble or sparingly soluble.

Example XVII

a. Preparation of (dimethylaminoethyl)dicyclohexylcyclopentadiene

Under a nitrogen atmosphere, a solution of n-butyllithium in hexane (18.7 mL; 1.6 mol/L; 30 mmol) was added dropwise to a cooled (0°C) solution of dicyclohexyl-cyclopentadiene (Example IV) (6.90 g; 30.0 mmol) in dry tetrahydrofuran (125 ml) in a 250 ml three-necked round-bottomed flask provided with a magnetic stirrer and a dropping funnel. After 24 hours' stirring at room temperature, 30.0 mmol of 2-(dimethylaminoethyl) tosylate prepared in situ were added. After 18 hours' stirring the conversion was found to be 88%, and water (100 ml) was carefully added dropwise to the reaction mixture and the tetrahydrofuran was then distilled off. The crude product was extracted with ether and the combined organic phase was then dried (sodium sulphate) and evaporated to dryness. The residue was purified on a silica gel column, which resulted in 7.4 g of (dimethylaminoethyl)dicyclohexylcyclopentadiene.

b. Synthesis of 1-(dimethylaminoethyl)-2,4-dicyclohexylcyclopentadienyltitanium(III) dichloride and [1-(dimethylaminoethyl)-2,4-dicyclohexylcyclopentadienyl]dimethyltitanium(III)

$[\text{C}_5\text{H}_2(\text{C}-\text{C}_6\text{H}_{11})_2(\text{CH}_2)_2\text{NMe}_2\text{Ti(III)Cl}_2]$ and $[\text{C}_5\text{H}_2(\text{C}-\text{C}_6\text{H}_{11})_2(\text{CH}_2)_2\text{NMe}_2\text{Ti(III)Me}_2]$

In a Schlenk vessel, 1.37 g (4.54 mmol) of (dimethylaminoethyl)dicyclohexylcyclopentadiene were dissolved in 30 mL of diethyl ether and the solution was then cooled to -60°C. Then 2.84 mL of n-butyllithium (1.6M in hexane; 4.54 mmol) were added dropwise. The reaction mixture was slowly brought to room temperature, followed by stirring for 2 hours. After evaporation of the solvent a yellow powder remained to which 30 mL of petroleum ether were added. In a second Schlenk vessel 40 mL of tetrahydrofuran were added to 1.68 g of $\text{Ti(III)Cl}_3 \cdot 3\text{THF}$ (4.53 mmol). Both Schlenk vessels were cooled to -60°C and the organolithium compound was then added to the Ti(III)Cl_3 suspension. The reaction mixture was then stirred for 18 hours at room temperature, after which the solvent was evaporated. To the residue 50 mL of petroleum ether were added, which was subsequently evaporated to dryness. A green solid remained containing 1-(dimethylaminoethyl)-2,4-dicyclohexylcyclopentadienyltitanium(III) dichloride.

In a Schlenk vessel, 0.31 g (0.671 mmol) of the above-described 1-(dimethylaminoethyl)-2,4-dicyclohexylcyclopentadienyltitanium(III) dichloride was dissolved in 30 mL of diethyl ether. The solution was cooled to -60°C and 0.73 mL (1.84M in diethyl ether; 1.34 mmol) of methyl lithium was then added dropwise. The solution was slowly brought to room temperature, followed by stirring for 1 hour. Then the solvent was evaporated and the residue extracted with 40 mL of

petroleum ether. The filtrate was boiled down and dried for 18 hours in vacuo. There remained 0.14 g of a black/brown oil containing [1-(dimethylaminoethyl)-2,4-dicyclohexylcyclopentadienyl] dimethyltitanium(III).

Example XVIII

a. Preparation of (dimethylaminoethyl)di(2-pentyl)cyclopentadiene

Under a nitrogen atmosphere, a solution of n-butyllithium in hexane (24.0 ml; 1.6 mol/L; 38 mmol) was added dropwise to a cooled (0°C) solution of di-(2-pentyl)cyclopentadiene (7.82 g; 38.0 mmol) in dry tetrahydrofuran (125 ml) in a 250 ml three-necked round-bottomed flask provided with a magnetic stirrer and a dropping funnel. After 24 hours' stirring at room temperature, 2-(dimethylaminoethyl) tosylate (38.0 mmol) prepared in situ was added. After 18 hours' stirring the conversion was found to be 92%, and water (100 ml) was carefully added dropwise to the reaction mixture and the tetrahydrofuran was then distilled off. The crude product was extracted with ether and the combined organic phase was then dried (sodium sulphate) and evaporated to dryness. The residue was purified on a silica gel column, which resulted in 8.2 g of (dimethylaminoethyl)di(2-pentyl)cyclopentadiene.

b. Synthesis of 1-(dimethylaminoethyl)-2,4-di(2-pentyl)cyclopentadienyltitanium(III) dichloride and [1-(dimethylaminoethyl)-2,4-di(2-pentyl)cyclopentadienyl]dimethyltitanium(III)

[C₅H₂(2-C₅H₁₁)₂(CH₂)₂NMe₂Ti(III)Cl₂] and [C₅H₂(2-C₅H₁₁)₂(CH₂)₂NMe₂Ti(III)Me₂]

In a Schlenk vessel, 1.60 g (5.77 mmol) of (dimethylaminoethyl)di(2-pentyl)cyclopentadiene were dissolved in 40 mL of diethyl ether and the solution was then cooled to -60°C. Then 3.6 mL of n-butyllithium (1.6M in hexane; 5.77 mmol) were added dropwise. The reaction mixture was slowly brought to room temperature, followed by stirring for 2 hours. In a second Schlenk vessel 40 mL of tetrahydrofuran were added to 2.14 g of Ti(III)Cl₃·3THF (5.77 mmol). Both Schlenk vessels were cooled to -60°C and the organolithium compound was then added to the Ti(III)Cl₃ suspension. The reaction mixture was then stirred for 18 hours at room temperature, after which the solvent was evaporated. To the residue 50 mL of petroleum ether were added, which was subsequently evaporated to dryness. 1.60 g of a green solid remained containing 1-(dimethylaminoethyl)-2,4-di(2-pentyl)cyclopentadienyltitanium(III) dichloride.

In a Schlenk vessel, 0.33 g (0.835 mmol) of 1-(dimethylaminoethyl)di(2-pentyl)cyclopentadienyltitanium(III) dichloride was dissolved in 40 mL of diethyl ether. The solution was cooled to -60°C and 0.90 mL of methylolithium (1.84M in diethyl ether; 1.66 mmol) was then added dropwise. The reaction mixture was slowly brought to room temperature, followed by stirring for 1 hour. Then the solvent was evaporated. The residue was extracted with 50 mL of petroleum ether, and the filtrate was then boiled down. There remained 0.24 g of a black/brown oil containing [1-(dimethylaminoethyl)-2,4-di(2-pentyl)cyclopentadienyl]dimethyltitanium(III).

Example XIX

a. Preparation of (dimethylaminoethyl)tri(2-propyl)cyclopentadiene

In a dry 500 mL three-necked flask with a magnetic stirrer, a solution of 62.5 mL of n-butyllithium (1.6M in n-hexane; 100 mmol) was added under a dry nitrogen atmosphere to a solution of 19.2 g (100 mmol) of triisopropyl-cyclopentadiene in 250 mL of THF at -60°C. After heating to room temperature (in approximately 1 hour) stirring continued for a further 2 hours. After cooling to -60°C, a solution of (dimethylaminoethyl) tosylate (105 mmol) prepared in situ was added over a period of 5 minutes. The reaction mixture was heated to room temperature, followed by overnight stirring. After addition of water, the product was extracted with petroleum ether (40-60°C). The combined organic layer was dried (Na₂SO₄) and evaporated under reduced pressure. The conversion was greater than 95%. The yield of product after distillation (based on triisopropyl-cyclopentadiene) was approximately 55%.

b. Synthesis of 1-(dimethylaminoethyl)-2,3,5-tri(2-propyl)cyclopentadienyltitanium(III) dichloride and [1-(dimethylaminoethyl)-2,3,5-tri(2-propyl)cyclopentadienyl]dimethyltitanium(III)

[C₅H(iPr)₃(CH₂)₂NMe₂Ti(III)Cl₂] and [C₅H(iPr)₃(CH₂)₂NMe₂Ti(III)Me₂]

In a 500 mL 3-necked flask 200 mL of petroleum ether were added to 8.5 g (28.18 mmol) of the potassium 1-(dimethylaminoethyl)-2,3,5-tri(2-propyl)cyclopentadienyl. In a second (1 L) 3-necked flask, 300 ml of tetrahydrofuran were added to 10.5 g (28.3 mmol) of Ti(III)Cl₃·3THF. Both flasks were cooled to -60°C and the organopotassium compound was then added to the Ti(III)Cl₃ suspension. The reaction mixture containing 1-(dimethylaminoethyl)-2,3,5-tri(2-propyl)cyclopentadienyltitanium(III) dichloride was slowly brought to room temperature, after which stirring was continued for a further 18 hours. This was followed by cooling to -60°C and 30.6 mL of methylolithium (1.827 M in diethyl ether, 55.9 mmol) were then added. After 2 hours' stirring at room temperature, the solvent was removed and the residue was

dried in vacuo for 18 hours. To the product, 700 mL of petroleum ether were then added, followed by filtration. The filtrate was boiled down and dried in vacuo for 2 days. There remained 9.2 g of a brown/black oil containing [1-(dimethylaminoethyl)-2,3,5-tri(2-propyl)cyclopentadienyl]dimethyltitanium(III).

5 Example XX

a. Preparation of (di-n-butylaminoethyl)di(2-pentyl)cyclopentadiene

The reaction was carried out in a manner identical to that for (dimethylaminoethyl)-di-(2-pentyl)cyclopentadiene, the tosylate of N,N-di-n-butylaminoethanol being prepared in situ. The conversion was 88%. The di-(n-butylaminoethyl)-di-(2-pentyl)cyclopentadiene was obtained, after preparative column purification on silica gel using, successively, petroleum ether (40-60°C) and THF, followed by distillation under reduced pressure, in a yield of 51%.

b. Preparation of 1-(di-n-butylaminoethyl)-2,4-di(2-pentyl)cyclopentadienyltitanium(III) dichloride

15 $[\text{C}_5\text{H}_2(2\text{-C}_5\text{H}_{11})_2(\text{CH}_2)_2\text{N}(\text{n-C}_4\text{H}_9)_2\text{Ti(III)Cl}_2]$

In a Schlenk vessel, 0.919 g (2.54 mmol) of (di-n-butylaminoethyl)di(2-pentyl)cyclopentadiene was dissolved in 40 mL of diethyl ether and the solution was then cooled to -60°C. 1.6 mL of n-butyllithium (1.6M in hexane; 2.56 mmol) was then added dropwise. The reaction mixture was slowly brought to room temperature, followed by 2 hours' stirring. This was then added, at -60°C, to 960 mg (2.59 mmol) of $\text{Ti(III)Cl}_3 \cdot 3\text{THF}$ in 20 mL of tetrahydrofuran. The reaction mixture was then stirred for 18 hours at room temperature, after which the solvent was evaporated. The residue was washed with 10 mL. There remained 0.95 g of a green solid containing 1-(di-n-butylaminoethyl)-2,4-di(2-pentyl)cyclopentadienyltitanium(III) dichloride.

25 Example XXI

a. Preparation of (dimethylaminoethyl)di(2-propyl)cyclopentadiene

The reaction was carried out in a manner identical to that for (dimethylaminoethyl)tri(2-propyl)cyclopentadiene. The conversion was 97%. The dimethylaminoethyldiisopropylcyclopentadiene was obtained by distillation, with a yield of 54%.

b. Synthesis of [1-(dimethylaminoethyl)-2,4-di(2-propyl)cyclopentadienyltitanium(III) dichloride and [1-(dimethylaminoethyl)-2,4-di(2-propyl)cyclopentadienyl]dimethyltitanium(III)]

35 $[\text{C}_5\text{H}_2(\text{iPr})_2(\text{CH}_2)_2\text{NMe}_2\text{Ti(III)Cl}_2]$ and $[\text{C}_5\text{H}_2(\text{iPr})_2(\text{CH}_2)_2\text{NMe}_2\text{Ti(III)Me}_2]$

To 8.9 g (40.3 mmol) of (dimethylaminoethyl)di-(2-propyl)cyclopentadiene in 100 mL of tetrahydrofuran in a 250 mL 3-necked flask, 25.2 mL of n-butyllithium (1.6M, 40.3 mmol) were added dropwise. In a second (500 mL) 3-necked flask, 100 mL of tetrahydrofuran were added to 14.93 g (40.3 mmol) of $\text{Ti(III)Cl}_3 \cdot 3\text{THF}$. Both flasks were cooled to -60°C and the organolithium compound was then added to the Ti(III)Cl_3 suspension. The reaction mixture containing 1-(dimethylaminoethyl)-2,4-di(2-propyl)cyclopentadienyltitanium(III) dichloride was slowly brought to room temperature, after which stirring was continued for a further 18 hours. This was followed by cooling to -60°C, and 50.4 mL of methylolithium (1.6M in diethyl ether; 80.6 mmol) were then added. After 2 hours' stirring at room temperature, the solvent was removed and the residue was dried in vacuo for 18 hours. To the product, 350 mL of petroleum ether were then added, followed by filtration. The filtrate was boiled down and dried in vacuo for one day. There remained 11.6 g of a brown/black oil containing [1-(dimethylaminoethyl)-2,4-di(2-propyl)cyclopentadienyl] dimethyltitanium(III).

Example XXII

a. Preparation of (dimethylaminoethyl)di(2-butyl)cyclopentadiene

Under a nitrogen atmosphere, a solution of n-butyllithium in hexane (31.2 mL; 1.6 mol/L; 50 mmol) was added dropwise to a cooled (0°C) solution of di-(2-butyl)cyclopentadiene (8.90 g; 50.0 mmol) in dry tetrahydrofuran (150 mL) in a 250 mL three-necked round-bottomed flask provided with a magnetic stirrer and a dropping funnel. After 24 hours' stirring at room temperature, the 2-(dimethylaminoethyl) tosylate (50.0 mmol) was added. After 18 hours' stirring the conversion was found to be 96%, and water (100 mL) was carefully added dropwise to the reaction mixture and the tetrahydrofuran was then distilled off. The crude product was extracted with ether and the combined organic phase was then dried (sodium sulphate) and boiled down. The residue was purified on a silica gel column, which resulted in 8.5 g of (dimethylaminoethyl)di(2-butyl)cyclopentadiene.

b. Synthesis of 1-(dimethylaminoethyl)-2,4-di(2-butyl)cyclopentadienyltitanium(III) dichloride and [1-(dimethylaminoethyl)-2,4-di(2-butyl)cyclopentadienyl]dimethyltitanium(III)

$[C_5H_2(2-C_4H_9)_2(CH_2)_2NMe_2Ti(III)Cl_2]$ and $[C_5H_2(2-C_4H_9)_2(CH_2)_2NMe_2Ti(III)Me_2]$

In a Schlenk vessel, 2.36 g (9.48 mmol) of (dimethylaminoethyl)di(2-butyl)cyclopentadiene was dissolved in 50 mL of diethyl ether and the solution then cooled to $-60^\circ C$. Then 5.9 mL of n-butyllithium (1.6M in hexane; 9.44 mmol) were added dropwise. The reaction mixture was slowly brought to room temperature, followed by stirring for 2 hours. In a second Schlenk vessel 50 mL of tetrahydrofuran were added to 3.51 g of $Ti(III)Cl_3 \cdot 3THF$ (9.44 mmol). Both Schlenk vessels were cooled to $-60^\circ C$ and the organolithium compound was then added to the $Ti(III)Cl_3$ suspension. The reaction mixture was then stirred for 18 hours at room temperature, after which the solvent was evaporated. To the residue 50 mL of petroleum ether were added, which was subsequently evaporated to dryness. 2.15 g of a green solid remained containing 1-(dimethylaminoethyl)-2,4-di(2-butyl)cyclopentadienyltitanium(III) dichloride.

In a Schlenk vessel, 0.45 g (1.22 mmol) of 1-(dimethylaminoethyl)di(2-butyl)cyclopentadienyltitanium(III) dichloride was dissolved in 40 mL of diethyl ether. The solution was cooled to $-60^\circ C$ and 1.33 mL of methylolithium (1.84M in diethyl ether; 2.44 mmol) were then added dropwise. The reaction mixture was slowly brought to room temperature, followed by stirring for 1 hour. Then the solvent was evaporated. The residue was extracted with 50 mL of petroleum ether, and the filtrate was boiled down. There remained 0.36 g of a black/brown oil containing [1-(dimethylaminoethyl)-2,4-di(2-butyl)cyclopentadienyl]dimethyltitanium(III).

Example XXIII

a. Preparation of (dimethylaminoethyl)tri(2-butyl)cyclopentadiene

The reaction was carried out in a manner identical to that for (dimethylaminoethyl)tri(2-propyl)cyclopentadiene. The conversion was 92%. The product was obtained by distillation, with a yield of 64%.

b. Synthesis of [1-(dimethylaminoethyl)-2,3,5-tri(2-butyl)cyclopentadienyl]titanium(III) dichloride and [1-(dimethylaminoethyl)-2,3,5-tri(2-butyl)cyclopentadienyl]dimethyltitanium(III)

$[C_5H(2-C_4H_9)_3(CH_2)_2NMe_2Ti(III)Cl_2]$ and $[C_5H(2-C_4H_9)_3(CH_2)_2NMe_2Ti(III)Me_2]$

In a 500 mL 3-necked flask 200 mL of petroleum ether were added to 6.28 g (20.6 mmol) of the potassium 1-(dimethylaminoethyl)-2,3,5-tri(2-butyl)cyclopentadienyl. In a second (1 L) 3-necked flask, 300 mL of tetrahydrofuran were added to 7.65 g (20.6 mmol) of $Ti(III)Cl_3 \cdot 3THF$. Both flasks were cooled to $-60^\circ C$ and the organopotassium compound was then added to the $Ti(III)Cl_3$ suspension. The reaction mixture containing 1-(dimethylaminoethyl)-2,3,5-tri(2-butyl)cyclopentadienyltitanium(III) dichloride was slowly brought to room temperature, after which stirring was continued for a further 18 hours. This was followed by cooling to $-60^\circ C$ and 22.3 mL of methylolithium (1.827 M in diethyl ether; 40.7 mmol) were then added. After 2 hours' stirring at room temperature, the solvent was removed and the residue was dried in vacuo for 18 hours. To the product, 700 mL of petroleum ether were then added, followed by filtration. The filtrate was boiled down and dried in vacuo for 2 days. There remained 7.93 g of a brown/black oil containing [1-(dimethylaminoethyl)-2,3,5-tri(2-butyl)cyclopentadienyl]dimethyltitanium(III).

Example XXIV

Preparation of (dimethylaminoethyl)di(3-pentyl)cyclopentadiene

The reaction was carried out in a manner identical to that for (dimethylaminoethyl)di(2-propyl)cyclopentadiene. The conversion was 99%. The (dimethylaminoethyl)di(3-pentyl)cyclopentadiene was obtained after preparative column purification on silica gel using, successively, petroleum ether (40-60°C) and THF, the yield being 85%.

Example XXV

Preparation of (di-n-butylaminoethyl)-di-(3-pentyl)cyclopentadiene

The reaction was carried out in a manner identical to that for (di-n-butylaminoethyl)di(2-pentyl)cyclopentadiene. The conversion was 95%. The product was obtained after preparative column purification on silica gel using, successively, petroleum ether (40-60°C) and THF, the yield being 75%.

Example XXVIPreparation of (2-dimethylaminoethyl)-tri-(3-pentyl)cyclopentadiene

The reaction was carried out in a manner identical to that for (dimethylaminoethyl)tri(2-propyl)cyclopentadiene. The conversion was 94%. The (2-dimethylaminoethyl)-tri-(3-pentyl)cyclopentadiene was obtained after preparative column purification on silica gel using, successively, petroleum ether (40-60°C) and THF, the yield being 61%.

Example XXVIIa. Preparation of cyclohexyl(dimethylaminoethyl)-di-(2-propyl)cyclopentadiene

In a Schlenk vessel, at room temperature a solution of n-butyllithium in hexane (25.0 mL; 1.6 mol/L; 40.0 mmol) was added dropwise to a solution of cyclohexyldiisopropyl-cyclopentadiene (9.28 g; 40.0 mmol) in dry THF (150 mL). Then, in another Schlenk vessel, a solution of n-butyl-lithium in hexane (25.0 mL; 1.6 mol/L; 40.0 mmol) was added dropwise to a cold (-78°C) solution of dimethyl-aminoethanol (3.56 g; 40.0 mmol) in THF (100 mL). After an hour and a half's stirring at room temperature, the mixture was again cooled to -78°C and the solid tosyl chloride (8.10 g; 40.0 mmol) was added slowly. The mixture was brought to 0°C, being stirred for 5 minutes in the process, again cooled to -78°C, and then the mixture from the first Schlenk vessel was added all at once. After 16 hours' stirring at room temperature the conversion was 100%. After column chromatography 11.1 g of cyclohexyl(dimethylaminoethyl)-di-(2-propyl)cyclopentadiene were obtained.

b. Synthesis of 1-(dimethylaminoethyl)-4-cyclohexyl-2,5-di(2-propyl)cyclopentadienyltitanium(III) dichloride and [1-(dimethylaminoethyl)-4-cyclohexyl-2,5-di(2-propyl)cyclopentadienyl]dimethyltitanium(III)

[C₅H(c-Hex)(2-C₃H₇)₂(CH₂)₂NMe₂Ti(III)Cl₂] and [C₅H(c-Hex)(2-C₃H₇)₂(CH₂)₂NMe₂Ti(III)Me₂]

To lithium (dimethylaminoethyl)cyclohexyldi(2-propyl)cyclopentadiene (2.18 g, 7.20 mmol), dissolved in 20 mL of tetrahydrofuran, a cooled slurry (-70°C) of Ti(III)Cl₃·3THF (2.67 g, 7.20 mmol) in 20 mL of THF was added at -70°C. The dark-green solution formed was stirred for 72 hours at room temperature. After this had been boiled down, 30 mL of petroleum ether (40-60) were added. After evaporating to dryness once more, a green powder (2.37 g) was obtained, containing 1-(dimethylaminoethyl)-4-cyclohexyl-2,5-di(2-propyl)cyclopentadienyltitanium(III) dichloride[lithium chloride].

To a slurry, cooled to -70°C, of 0.63 g (1.36 mmol) of the [1-(dimethylaminoethyl)-4-cyclohexyl-2,5-di(2-propyl)cyclopentadienyltitanium(III) dichloride].[lithium chloride] obtained above in 30 mL of diethyl ether, 1.70 mL of methyl lithium (1.6 M in diethyl ether, (2.72 mmol) was added dropwise. The green-brown slurry immediately darkened. Then the mixture was stirred for 1 hour at room temperature, boiled down to dryness and dissolved in 40 mL of petroleum ether. After filtration and complete evaporation of the solvent a black powder (0.47 g, 1.22 mmol) was obtained containing 1-(dimethylaminoethyl)-4-cyclohexyl-2,5-di(2-propyl)cyclopentadienyltitanium(III) dimethyl.

Example XXVIIIPreparation of (di-n-butylaminoethyl)di(2-propyl)cyclopentadiene

The reaction was carried out in a manner identical to that for (dimethylaminoethyl)di(2-propyl)cyclopentadiene, the tosylate of N,N-di-n-butylaminoethanol being prepared in situ. The conversion was 94%. The non-geminal di-n-butylaminoethyldi(2-propyl)cyclopentadiene was obtained by distillation with a yield of 53%.

Example XXIXPreparation of (dimethylaminoethyl)-tri-(2-pentyl)cyclopentadiene

The reaction was carried out in a manner identical to that for (dimethylaminoethyl)tri(2-propyl)cyclopentadiene. The conversion was 90%. The (dimethylaminoethyl)-tri-(2-pentyl)cyclopentadiene was obtained after preparative column purification on silica gel using, successively, petroleum ether (40-60°C) and THF, the yield being 57%.

Example XXXa. Preparation of bis(dimethylaminoethyl)triisopropylcyclopentadiene

5 In a dry 500 mL three-necked flask with a magnetic stirrer, a solution of 62.5 mL of *n*-butyllithium (1.6 M in *n*-hexane; 100 mmol) was added under a dry nitrogen atmosphere to a solution of 19.2 g (100 mmol) of triisopropylcyclopentadiene in 250 mL of THF at -60°C. After heating to room temperature (in approximately 1 hour) stirring continued for a further 2 hours. After cooling to -60°C, a solution of (dimethylaminoethyl) tosylate (105 mmol) prepared in situ was added over a period of 5 minutes. The reaction mixture was heated to room temperature, followed by overnight stirring.

10 After addition of water, the product was extracted with petroleum ether (40-60°C). The combined organic layer was dried (Na₂SO₄) and evaporated to dryness under reduced pressure. The conversion was greater than 95%. A portion of the product thus obtained (10.1 g; 38.2 mmol) was again alkylated under the same conditions with (dimethylaminoethyl)tosylate (39.0 mmol). The bis(2-dimethylaminoethyl)triisopropylcyclopentadiene was obtained with a yield of 35% via column chromatography.

15 b. Synthesis of [1,3-bis(dimethylaminoethyl)-2,4,5-tri(2-propyl)cyclopentadienyl]titanium(III) dichloride and [1,3-bis(dimethylaminoethyl)-2,4,5-tri(2-propyl)cyclopentadienyl]dimethyltitanium(III)
 $[C_5(2-C_3H_7)_3((CH_2)_2NMe_2)_2Ti(III)Cl_2]$ and $[C_5(2-C_3H_7)_3((CH_2)_2NMe_2)_2Ti(III)Me_2]$

20 In a 500 mL 3-necked flask 200 mL of petroleum ether were added to 3.38 g (10.1 mmol) of the potassium 1,3-bis(dimethylaminoethyl)-2,4,5-tri(2-propyl)cyclopentadienyl. In a second (1 L) 3-necked flask, 300 mL of tetrahydrofuran were added to 3.75 g (10.1 mmol) of Ti(III)Cl₃·3THF. Both flasks were cooled to -60°C and the organopotassium compound was then added to the Ti(III)Cl₃ suspension. The reaction mixture containing 1-(dimethylaminoethyl)-2,3,5-tri(2-propyl)cyclopentadienyltitanium(III) dichloride was slowly brought to room temperature, after which stirring was continued for a further 18 hours. This was followed by cooling to -60°C and 11.0 mL of methylolithium (1.827 M in diethyl ether; 20.1 mmol) were then added. After 2 hours' stirring at room temperature, the solvent was removed and the residue was dried in vacuo for 18 hours. To the product, 700 mL of petroleum ether were then added, followed by filtration. The filtrate was boiled down and dried in vacuo for 2 days. There remained 3.62 g of a brown/black oil containing [1,3-bis(dimethylaminoethyl)-2,4,5-tri(2-propyl)cyclopentadienyl]dimethyltitanium(III).

30 Example XXXI

a. Preparation of (dimethylaminoethyl)tricyclohexylcyclopentadiene

35 The reaction was carried out in a manner identical to that for (dimethylaminoethyl)dicyclohexylcyclopentadiene. The conversion was 91%. The product was obtained via preparative column purification on silica gel using, successively, petroleum ether (40-60°C) and THF as the eluent, the yield being 80%.

40 b. Synthesis of 1-(dimethylaminoethyl)-2,3,5-tricyclohexylcyclopentadienyltitanium(III) dichloride and [1-(dimethylaminoethyl)-2,3,5-tricyclohexylcyclopentadienyl]dimethyltitanium(III)
 $[C_5H(c-Hex)_3(CH_2)_2NMe_2Ti(III)Cl_2]$ and $[C_5H(c-Hex)_3(CH_2)_2NMe_2Ti(III)Me_2]$

To lithium (dimethylaminoethyl)tricyclohexylcyclopentadiene (2.11 g, 5.70 mmol), dissolved in 20 mL of tetrahydrofuran, a cooled slurry (-70°C) of Ti(III)Cl₃·3THF (2.11 g, 5.70 mmol) in 20 mL of THF was added at -70°C. The dark-green solution formed was stirred for 72 hours at room temperature. After this had been boiled down, 30 mL of petroleum ether (40-60°C) were added. After evaporating to dryness once more, a mint-green powder (2.80 g) was obtained, containing 1-(dimethylaminoethyl)-2,3,5-tricyclohexylcyclopentadienyltitanium(III) dichloride. To a slurry, cooled to -70°C, of 0.50 g (0.922 mmol) of the [1-(dimethylaminoethyl)-2,3,5-tricyclohexylcyclopentadienyl-titanium(III) dichloride], [lithium chloride] obtained above in 30 mL of diethyl ether, 1.15 mL of methylolithium (1.6 M in diethyl ether, 1.84 mmol) was added dropwise. The green-brown slurry immediately darkened. Then the mixture was stirred for 1 hour at room temperature, boiled down to dryness and dissolved in 40 mL of petroleum ether. After filtration and complete evaporation of the solvent a black powder (0.40 g, 0.87 mmol) was obtained containing 1-(dimethylaminoethyl)tricyclohexylcyclopentadienyl-Ti(III)dimethyl.

55 Example XXXII

a. Preparation of (di-n-butylaminoethyl)-tri-(2-pentyl)cyclopentadiene

The reaction was carried out in a manner identical to that for (di-n-butylaminoethyl)-di-(3-pentyl)cyclopentadiene.

The conversion was 88%. The (2-di-n-butylaminoethyl)-di-(2-pentyl)cyclopentadiene was obtained after preparative column purification on silica gel using, successively, petroleum ether (40-60°C) and THF, followed by distillation under reduced pressure, the yield being 51%.

5 b. Synthesis of 1-(di-n-butylaminoethyl)-2,3,5-tri(2-pentyl)cyclopentadienyltitanium(III) dichloride
 $[C_5H(2-C_5H_9)_3(CH_2)_2N(n-Bu)_2Ti(III)Cl_2]$

2.633 g (6.11 mmol) of (di-n-butylaminoethyl)tri-(2-pentyl)cyclopentadiene were dissolved in 50 mL of diethyl ether and cooled to -78°C. Then 3.8 mL of n-butyllithium (1.6 M in hexane; 6.11 mmol) were added. After stirring for 18 hours
 10 at room temperature, the clear pale-yellow solution was boiled down followed by washing once with 25 mL of petroleum ether. The solvent was then completely evaporated, leaving behind 1.58 g of a yellow oil containing lithium 1-(di-n-butylaminoethyl)-2,3,5-tri(2-pentyl)cyclopentadienyl. Then the organolithium compound was dissolved in 50 mL of tetrahydrofuran and added, at -78°C, to 9.23 g (24.9 mmol) of $Ti(III)Cl_3 \cdot 3THF$ in 50 mL of tetrahydrofuran. After 18 hours'
 15 stirring at room temperature a dark-green solution had formed. After this solution had been completely boiled down, 1.52 g of a green oil remained, containing 1-(di-n-butylaminoethyl)-2,3,5-tri(2-pentyl)cyclopentadienyl-titanium(III) dichloride.

Example XXXIII

20 a. Preparation of (dimethylaminoethyl)tetraethylcyclopentadiene

In a Schlenk vessel, a solution of n-butyllithium in hexane (6.00 mL; 1.65 mol/L; 9.90 mmol) was added dropwise to a solution of tetraethylcyclopentadiene (2.066 g; 11.6 mmol) in dry THF (20 mL) at room temperature.

Then, in a second Schlenk vessel, a solution of n-butyllithium in hexane (5.90 mL; 1.65 mol/L; 9.74 mmol) was
 25 added dropwise to a cold (-78°C) solution of 2-dimethyl-aminoethanol (0.867 g; 9.74 mmol) in THF (35 mL). After two hours' stirring at room temperature, the mixture was again cooled to -78°C and the solid tosyl chloride (1.855 g; 9.74 mmol) was added slowly. The mixture was brought to 0°C, being stirred for 5 minutes in the process, and the mixture from the first Schlenk vessel was then added all at once. After 16 hours the conversion was 100%. After column chromatography 2.6 g of (dimethylaminoethyl)tetraethylcyclopentadiene were obtained.

30

b. Synthesis of 1-(dimethylaminoethyl)-2,3,4,5-tetraethylcyclopentadienyltitanium(III) dichloride and [1-(dimethylaminoethyl)-2,3,4,5-tetraethylcyclopentadienyl]dimethyl-titanium(III)
 $[C_5Et_4(CH_2)_2NMe_2Ti(III)Cl_2]$ and $[C_5Et_4(CH_2)_2NMe_2Ti(III)Me_2]$

35 In a Schlenk vessel, 0.38 g of (dimethylaminoethyl)tetraethylcyclopentadiene (1.523 mmol) was dissolved in 20 mL of diethyl ether and the solution was then cooled to -60°C. Then 0.95 mL of n-butyllithium (1.6 M in hexane; 1.52 mmol) were added dropwise. After 30 minutes, cooling was stopped, followed by 1 hour's stirring at room temperature. In a second Schlenk vessel 30 mL of tetrahydrofuran were added to 0.57 g (1.538 mmol) of $Ti(III)Cl_3 \cdot 3THF$. Both Schlenk
 40 vessels were cooled to -60°C and the organolithium compound was then added to the $Ti(III)Cl_3$ suspension. The reaction mixture was then stirred for 18 hours at room temperature, after which the solvent was evaporated. To the residue 50 mL of petroleum ether were added, which was subsequently evaporated to dryness. The residue was a green solid containing 1-(dimethylaminoethyl)-2,3,4,5-tetraethylcyclopentadienyltitanium(III) dichloride.

20 mL of diethyl ether were added to 0.25 g (0.68 mmol) of the product. After cooling to -60°C, 0.85 mL of methyl-
 45 lithium (1.6 M in diethyl ether; 1.36 mmol) was added, followed by three hours' stirring at room temperature. Then the solvent was removed under reduced pressure. After addition of petroleum ether, filtration and boiling down, 0.17 g of a dark oil was obtained, containing 1-[(dimethyl-aminoethyl)-2,3,4,5-tetraethylcyclopentadienyl]dimethyltitanium(III).

Example XXXIV

50 a. Preparation of (dimethylaminoethyl)tetra-n-octylcyclopentadiene

In a Schlenk vessel, a solution of n-butyllithium in hexane (24.8 mL; 1.6 mol/L; 39.6 mmol) was added dropwise to a solution of tetra-n-octylcyclopentadiene (20.4 g; 39.6 mmol) in dry THF (100 mL) at room temperature.

Then, in a second Schlenk vessel, a solution of n-butyllithium in hexane (24.6 mL; 1.6 mol/L; 39.6 mmol) was added
 55 dropwise to a cold (-78°C) solution of 2-dimethylaminoethanol (3.53 g; 39.6 mmol) in THF (30 mL). After two hours' stirring at room temperature, the mixture was again cooled to -78°C and the solid tosyl chloride (7.54 g; 39.6 mmol) was added slowly. The mixture was brought to 0°C, being stirred for 5 minutes in the process, and the mixture from the first Schlenk vessel was then added all at once. After 16 hours the conversion was 87%. After column chromatography 19.2 g of (dimethylaminoethyl)tetra-n-octyl-cyclopentadiene were obtained.

Example XXXVa. Preparation of (dimethylaminoethyl)tetra-n-propylcyclopentadiene

In a 500 mL 3-neck flask, a solution of n-butyllithium in hexane (93.8 mL; 1.6 mol/L; 150 mmol) was added dropwise to a solution of tetra-n-propylcyclopentadiene (35.0 g; 150 mmol) in dry THF (200 mL) at room temperature.

Then, in a second Schlenk vessel, a solution of n-butyllithium in hexane (93.8 mL; 1.6 mol/L; 150 mmol) was added dropwise to a cold (-78°C) solution of 2-dimethylaminoethanol (13.35 g; 150 mmol) in THF (100 mL). After two hours' stirring at room temperature, the mixture was again cooled to -78°C and the solid tosyl chloride (28.5 g; 150 mmol) was added slowly. The mixture was brought to -20°C, being stirred for 5 minutes in the process, and the mixture from the first Schlenk vessel was then added. After 16 hours the conversion was 97%. After column chromatography 39.6 g of (dimethylaminoethyl)tetra-n-propylcyclopentadiene were obtained.

b. Synthesis of 1-(dimethylaminoethyl)-2,3,4,5-tetra-n-propylcyclopentadienyltitanium(III) dichloride and [1-(dimethylaminoethyl)-2,3,4,5-tetra-n-propylcyclopentadienyl]dimethyltitanium(III)
 $[C_5(n\text{-Pr})_4(CH_2)_2NMe_2Ti(III)Cl_2]$ and $[C_5(n\text{-Pr})_4(CH_2)_2NMe_2Ti(III)Me_2]$

In a Schlenk vessel, 0.62 g of (dimethylaminoethyl)tetra(n-propyl)cyclopentadiene (2.03 mmol) was dissolved in 20 mL of diethyl ether and the solution was then cooled to -60°C. Then 1.27 mL of n-butyllithium (1.6 M in hexane; 2.03 mmol) were added dropwise. After 30 minutes cooling was stopped, followed by 1 hour's stirring at room temperature. In a second Schlenk vessel 30 mL of tetrahydrofuran were added to 0.75 g (2.03 mmol) of $Ti(III)Cl_3 \cdot 3THF$. Both Schlenk vessels were cooled to -60°C and the organolithium compound was then added to the $Ti(III)Cl_3$ suspension. The reaction mixture was then stirred for 18 hours at room temperature, after which the solvent was evaporated. To the residue 50 mL of petroleum ether were added, which was subsequently evaporated to dryness. The residue was a green oil containing 1-(dimethylaminoethyl)-2,3,4,5-tetra-n-propylcyclopentadienyltitanium(III) dichloride. 20 mL of diethyl ether were added to 0.51 g (1.01 mmol) of the product. After cooling to -60°C, 1.26 mL of methylolithium (1.6 M in diethyl ether; 2.02 mmol) was added, followed by three hours' stirring at room temperature. Then the solvent was removed under reduced pressure. After addition of petroleum ether, filtration and boiling down, 0.31 g of a dark oil was obtained, containing 1-[(dimethylaminoethyl)-2,3,4,5-tetra-n-propylcyclopentadienyl]dimethyltitanium(III)

Example XXXVIPreparation of (dimethylaminoethyl)di(2-phenylpropyl)cyclopentadiene

12.5 mL of a 1.6 molar solution of n-butyllithium in hexane was added dropwise to a cooled (0°C) solution of di-(2-phenyl-propyl)cyclopentadiene (6.05 g; 20.0 mmol) in dry tetrahydrofuran (100 mL) under a nitrogen atmosphere in a 250 mL three-necked round-bottomed flask provided with a magnetic stirrer and a dropping funnel. After 24 hours' stirring at room temperature, a solution of 2-(dimethyl-aminoethyl) tosylate (20.0 mmol), prepared in situ, in THF/hexane was added. After 18 hours' stirring the conversion was found to be 90%, and water (100 mL) was carefully added dropwise to the reaction mixture and the tetrahydrofuran was then distilled off. The crude product was extracted with ether and the combined organic phase was then dried (on sodium sulphate) and boiled down. The residue was purified on a silica gel column, which resulted in 5.98 grams (80%) of (dimethylaminoethyl)di(2-phenylpropyl)cyclopentadiene.

Example XXXVIIPreparation of ((dimethylaminoethyl)di(2-phenyl-propyl)cyclopentadienyl)titanium dichloride

To (dimethylaminoethyl)di(2-phenyl-propyl)cyclopentadiene (1.12 gram, 3 mmol), dissolved in 20 mL of tetrahydrofuran, 1.87 mL of a 1.6 molar butyllithium-in- hexane solution were added at 0°C (ice bath). After 15 minutes' stirring, this mixture was cooled further to -78°C, and a slurry, likewise cooled to -78°C, of $Ti(III)Cl_3 \cdot 3THF$ (1.11 g, 3 mmol) in 20 mL of THF was added. The cooling bath was removed, and the dark-green solution formed was stirred for 72 hours at room temperature. After this had been boiled down, 30 mL of petroleum ether (40-60) were added. After evaporation to dryness once more, a green powder (1.19 g) was obtained, containing ((dimethylaminoethyl)di(2-phenyl-propyl)cyclopentadienyl)titanium dichloride.

Example XXXVIIIa. Preparation of (dimethylaminoethyl)di(1,1-dimethylpropyl)cyclopentadiene

25 mL of a 1.6 molar solution of n-butyllithium in hexane was added dropwise to a cooled (0°C) solution of di(1,1-dimethyl-propyl)cyclopentadiene (8.25 g; 40.0 mmol) in dry tetrahydrofuran (125 ml) under a nitrogen atmosphere in a 250 ml three-necked round-bottomed flask provided with a magnetic stirrer and a dropping funnel. After 24 hours' stirring at room temperature, a solution of 2-(dimethylaminoethyl) tosylate (40.0 mmol), prepared in situ, in THF/hexane was added. After 18 hours' stirring the conversion was found to be 91%, and water (100 mL) was carefully added dropwise to the reaction mixture and the tetrahydrofuran was then distilled off. The crude product was extracted with ether and the combined organic phase was then dried (on sodium sulphate) and boiled down. The residue was purified on a silica gel column, which resulted in 9.1 grams (82%) of (dimethylaminoethyl)di(1,1-dimethyl-propyl)cyclopentadiene.

b. Synthesis of ((dimethylaminoethyl)di(1,1-dimethylpropyl)cyclopentadienyl)titanium dichloride

To (dimethylaminoethyl)di(1,1-dimethylpropyl)cyclopentadiene (1.39 gram, 5 mmol), dissolved in 20 mL of tetrahydrofuran, 3.1 mL of a 1.6 molar butyllithium-in-hexane solution were added at 0°C (ice bath). After 15 minutes' stirring, this mixture was cooled further to -78°C, and a slurry, likewise cooled to -78°C, of Ti(III)Cl₃·3THF (1.86 g, 5 mmol) in 20 mL of THF was added. The cooling bath was removed, and the dark-green solution formed was stirred for 72 hours at room temperature. After this had been boiled down, 30 mL of petroleum ether (40-60) were added. After evaporation to dryness once more, a green powder (1.68 g) was obtained, containing (dimethylaminoethyl)di(1,1-dimethyl-propyl)cyclopentadienyl)titanium dichloride.

Example XXXIXa. Preparation of (dimethylaminomethyl)di(1-methyl-1-ethylpropyl)cyclopentadiene

The preparation was carried out as in Example XXXVII, but now using 7.03 grams of di(1-methyl-1-ethyl-propyl)cyclopentadiene (30 mmol), 30 mol of 2-(dimethylaminoethyl) tosylate and 18.7 mL of 1.6 M butyllithium solution. In the first instance 90%, and after purification on the column 79% (7.24 grams), of (dimethylaminomethyl)di(1-methyl-1-ethyl-propyl)cyclopentadiene were obtained.

b. Synthesis of ((dimethylaminoethyl)di(1-methyl-1-ethyl-propyl)cyclopentadienyl)titanium dichloride

The synthesis was carried out as in Example XXXVIII, but now using: 1.53 grams of (dimethylaminomethyl)di(1-methyl-1-ethyl-propyl)cyclopentadiene. 1.76 grams of ((dimethylaminoethyl)di(1-methyl-1-ethyl-propyl)cyclopentadienyl)titanium dichloride were obtained.

Example XXXXPreparation of ligands from alkenyllithium compounds and estersPreparation of (N,N-di-n-decylaminoethyl)tetramethylcyclopentadiene

In a three-necked flask, 1.5 g (216 mmol) of Li wire were added to 200 mL of diethyl ether. The solution was cooled to 0°C, followed by slow dropwise addition of 10.0 mL (98 mmol) of 2-bromo-2-butene. Stirring continued at room temperature for 30 minutes. The solution became green/yellow in colour. Then the solution was cooled to -25°C and 13.05 grams (33.89 mmol) of N,N-di-n-decylaminoethyl propionate were slowly added dropwise with cooling. The temperature rose to 0°C. The reaction mixture was then stirred for a further 5 minutes at room temperature, followed by slow dropwise addition of 20 mL of water. The water and ether layers were separated, and the water layer was extracted with 2 x 50 mL of diethyl ether. The collected ether layer was dried (MgSO₄), filtered and boiled down. The residue was a pale-yellow liquid containing 4-(N,N-di-n-decylaminoethyl)-4-hydroxy-hepta-2,5-diene, which was characterized via NMR. The yield was 15.0 grams. In a three-necked flask, 10.0 grams of p-toluenesulphonic acid monohydrate (52.6 mmol) were dissolved in 150 mL of diethyl ether. To this, 15.0 g of the obtained carbinol (32.49 mmol) were added dropwise. During the dropwise addition a white suspension was formed. This was followed by two hours' stirring at room temperature. The solution was neutralized with Na₂CO₃ solution. The water and ether layers were separated, and the water layer was extracted with 2 x 50 mL of diethyl ether. The collected ether layers were dried, and the drying agent was filtered off. Then the diethyl ether was evaporated. The residue contained carbinol (30%) and ligand (70%). Yield: 11 grams of crude product (76%). 5 grams of this crude mixture were purified by column chromatography to give 3 g of pure ligand. According to this method, the following ligands were synthesized (Cp' = Me₄C₅; Et = (CH₂)₂):

	Cp'EtN(ethyl) ₂	: Yield (30%)
	(Et ₂)(Me ₂)C ₅ (CH ₂) ₂ NMe ₂	: Yield (15%)
	Cp'EtN(iButyl) ₂	: Yield (20%)
	Cp'CH(CH ₃)CH ₂ N(ethyl) ₂	: Yield (30%)
5	Cp'EtN(Me)Pr	: Yield (15%)
	Cp'EtN(n-Bu) ₂	: Yield (50%)
	Cp'EtN(cyclohexyl) ₂	: Yield (30%)
	Cp'EtN(secButyl) ₂	: Yield (15%)
	Cp'EtN(ethyl)(phenyl)	: Yield (10%)
10	Cp'EtN(iPropyl)(cyclohexyl)	: Yield (15%)
	Cp'EtN(Me)(ethylphenyl)	: Yield (25%)
	Cp'EtN(2-methoxyethyl) ₂	: Yield (25%)

Example XXXXI

15

a. Preparation of (N,N',N'-trimethyl-3,6-diazaheptyl)-
tetramethylcyclopentadiene

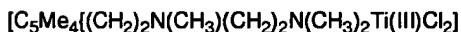
20

From 2-lithium-2-butene and EtOC(O)CH₂CH₂N(Me)CH₂CH₂NMe₂, the compound specified in the opening lines was prepared by the method described in DE-A-4303647, with a yield of 25% based on the amount of ester used as a starting material.

25

b. Synthesis of [1-(N,N',N'-trimethyl-3,6-diazaheptyl)-
2,3,4,5-tetramethylcyclopentadienyl]dichlorotitanium
(III)

30



In a Schlenk vessel, 0.21 g (0.838 mmol) of (N,N',N'-trimethyl-3,6-diazaheptyl)tetramethylcyclopentadiene was dissolved in 15 mL of tetrahydrofuran and the solution was then cooled to -60°C. Then 0.52 mL of n-butyllithium (1.6 M in hexane; 0.832 mmol) were added dropwise. After 2.5 hours cooling was stopped, followed by 30 minutes' stirring at room temperature. In a second Schlenk vessel 15 mL of tetrahydrofuran were added to 0.31 g (0.836 mmol) of Ti(III)Cl₃·3THF. Both Schlenk vessels were cooled to -60°C and the organolithium compound was then added to the Ti(III)Cl₃ suspension. After 2 hours cooling was stopped, followed by a further 2 hours' stirring at room temperature. Then the solvent was evaporated. To the residue containing [1-(N,N',N'-trimethyl-3,6-diazaheptyl)-2,3,4,5-tetramethylcyclopentadienyl]titanium(III) dichloride, 40 ml of petroleum ether were added which were subsequently evaporated again. The synthesized catalyst was not worked up further.

40

Example XXXXII

45

a. Preparation of 1-(N-methyl-N-(dioxolymethyl)ethyl)-2,3,4,5-tetramethylcyclopentadienyltitanium(III) dichloride
[C₅Me₄(CH₂)₂N(Me)(CH₂C₃H₅O₂)](Ti(III)Cl₂)

To 0.36 g (1.33 mmol) of lithium 1-(N-methyl-N-(dioxolymethyl)ethyl)-2,3,4,5-tetramethylcyclopentadienyl, 40 mL of petroleum ether were added in a Schlenk vessel.

50

To 0.50 g of Ti(III)Cl₃·3THF (1.35 mmol), 30 mL of tetrahydrofuran were added in a second Schlenk vessel. Both Schlenk vessels were cooled to -60°C, and the organolithium compound was then added to the Ti(III)Cl₃ suspension. The reaction mixture was stirred at room temperature for 18 hours and the solvent was then evaporated. 50 mL of petroleum ether were added to the residue, followed by evaporation once more. The residue was a green solid, containing 1-((N-methyl-N-(dioxolymethyl)ethyl)-2,3,4,5-tetramethylcyclopentadienyl)titanium(III) dichloride.

55

Example XXXXIIIa. Preparation of 1,2,3,4-tetramethyl-5(2-chloroethyl)cyclopentadiene

5 A 1-litre three-necked flask, provided with a dropping funnel, condenser, mechanical stirrer and nitrogen inlet, was charged with 30.5 g of 1,2,3,4-tetramethylcyclopentadiene (0.25 mol), dissolved in 700 mL of ethoxyethane, and cooled to 2°C. Then 160 ml of n-butyllithium (1.6 M in hexane; 0.26 mol) were added dropwise in 2 hours, followed by 18 hours' stirring at room temperature with the aid of a mechanical stirrer. Then 36.0 g of 1-bromo-2-chloroethane (0.25 mol) were added all at once. The reaction mixture was stirred at room temperature for 10 days. GC analysis of a sample showed
 10 that the conversion of the tetramethylcyclopentadiene was 91%. 100 ml of water were added to the reaction mixture, followed by separation of the water phase and the organic phase. The organic layer was washed once with 50 ml of saturated aqueous sodium chloride solution, dried (with sodium sulphate), filtered and boiled down. The residue (43.9 g) proved to have the following composition, according to gas chromatography (GC) analysis: apart from the starting materials 1-bromo-2-chloroethane (9 wt %) and 1,2,3,4-tetramethylcyclopentadiene (9 wt %), only non-geminally coupled product (84%) and geminally coupled product (16%) were found to be present.
 15

b. Preparation of 4,5,6,7-tetramethyl-spiro[2.4]-hepta-2,4-diene

The product obtained under a. (43.9 g), which according to GC analysis contains approximately 32 g of 1,2,3,4-tetramethyl-5(2-chloroethyl)cyclopentadiene (0.175 mol), was dissolved in 300 ml of THF. The solution was cooled to -60°C, followed by dropwise addition of 115 ml of n-butyllithium (1.6 M in hexane; 0.184 mol). The reaction mixture was brought to room temperature, followed by 40 hours' stirring.

The THF was evaporated and the residue was taken up in 200 ml of ethoxyethane. 100 ml of water were added and the water phase and organic phase were then separated. The organic phase was washed once with 100 ml of water.
 25 The combined water layer was extracted once with ethoxyethane. The combined organic layer was washed once with 50 ml of saturated sodium chloride solution, dried (sodium sulphate), filtered and boiled down. The residue (43.2 g) was a pale-yellow liquid which was purified with the aid of column chromatography (silica gel, mobile solvent petroleum ether). The yield was 24.2 g of a colourless liquid which was characterized with the aid of ¹H-NMR and by means of GC-MS as 4,5,6,7-tetramethyl-spiro[2.4]-hepta-2,4-diene. The yield was 93%, based on the amount of 1,2,3,4-tetramethyl-5(2-chloroethyl)cyclopentadiene used, and 65% based on 1,2,3,4-tetramethylcyclopentadiene.
 30

c. Synthesis of 1,2,3,4-tetramethyl-5(2-P,P-diphenylphosphinoethyl)cyclopentadiene

3.87 g of diphenylphosphine (21 mmol) were dissolved, in a 100 ml reactor, in 25 ml of THF and cooled to 2°C. Then 13.0 ml of n-butyllithium (1.6 M in hexane, 21 mmol) were added dropwise followed by stirring for half an hour at 2°C. Stirring then continued for 1 hour at room temperature. The dark-red mixture obtained was then cooled to -60°C. To this, 3.08 g of 4,5,6,7-tetramethyl-spiro[2.4]-hepta-2,4-diene (21 mmol) as obtained under b. were added all at once. The reaction mixture was brought to room temperature and stirred for 3 days. Then the THF was evaporated.

The residue, a yellow solid, was washed twice with petroleum ether at 0°C. The solid was then suspended in 50 ml of ethoxyethane and 5 ml of water were added dropwise. The ether layer and water layer were separated. The water layer was extracted a further 3 times with 25 ml of ethoxyethane. The combined ether layers were then boiled down, whereupon 4.72 g of a pale-brown, clear viscous liquid were obtained.

³¹P-NMR and ¹H-NMR analysis showed that the residue was 1,2,3,4-tetramethyl-5(2-P,P-diphenylphosphinoethyl)-cyclopentadiene. The yield of 1,2,3,4-tetramethyl-5(2-P,P-diphenylphosphinoethyl)cyclopentadiene, based on the 4,5,6,7-tetramethyl-spiro[2.4]-hepta-2,4-diene, was 67%. After GC analysis of the product, the purity was found to be >98%.
 45

d. Synthesis of 1,2,3,4-tetramethyl-5(2-P,P-dimethylphosphinoethyl)cyclopentadiene

50 Lithium dimethylphosphide was prepared by reaction of dimethylphenylphosphine and lithium, hydrolysis with water, distillation of dimethylphosphine and reaction of the latter with butyllithium (see Ta-shue Chou et al. in J. Org. Chem. 50, 4329 (1985)).

In a 250 ml reactor, 8.12 g of lithiumdimethylphosphide solution in THF (14 mmol) were mixed with 25 ml of THF. The solution obtained was cooled to -90°C. To this solution, 1.7 g of 4,5,6,7-tetramethyl-spiro[2.4]-hepta-2,4-diene (12 mmol) as obtained under b., was then added all at once. The reaction mixture was brought to room temperature and stirred for 2 days, followed by dropwise addition of 20 ml of water. Then the THF was evaporated and the residue was extracted with ether (ethoxyethane). The combined ether layers were boiled down and the residue distilled in vacuo.

The boiling point of the product was 51-52°C (at 0.01 mmHg). As ³¹P-NMR and ¹H-NMR analysis showed, the distilled product (1.13 g) was mainly 1,2,3,4-tetramethyl-5(2-P,P-dimethylphosphinoethyl)cyclopentadiene. The yield of

1,2,3,4-tetramethyl-5-(2-P,P-dimethylphosphinoethyl)-cyclopentadiene based on the 4,5,6,7-tetramethyl-spiro[2.4]-hepta-2,4-diene was 46%. After GC analysis the purity was found to be >95%.

Example XXXIV

a. Preparation of (1,2,3,4-tetramethylcyclopentadien-5-yl)chloromethyldimethylsilane.

In a 1500 ml reactor, 31.0 g of tetramethylcyclopentadiene (0.24 mol) were dissolved in 500 ml of tetrahydrofuran (THF) and cooled to 2°C. Then 160 ml of n-butyllithium (1.6M in hexane, 0.26 mol) were added dropwise, followed by stirring at room temperature for 18 hours with a mechanical stirrer. The reaction mixture obtained was cooled to -90°C. Then 36.3 g of chloromethyldimethylsilyl chloride (0.28 mol) were added all at once. Then the cooling bath was removed, the reaction mixture being allowed to come to room temperature, and being stirred, in total, for 18 hours. Then 200 ml of water were added. The THF was evaporated in a rotary evaporator, and the residue was extracted 3 times with 200 ml of ethoxyethane. The combined ether layers were dried on sodium sulphate, the sodium sulphate was filtered off, and the filtrate was boiled down. The residue (58.0 g) had a purity of >98% (determined by means of gas chromatography (GC)) of (1,2,3,4-tetramethylcyclopentadien-5-yl)chloromethyldimethylsilane.

b. Synthesis of (diphenylphosphinomethyl) (1,2,3,4-tetramethylcyclopentadien-5-yl)dimethylsilane

15.9 g of diphenylphosphine (85 mmol) were dissolved in 100 ml of ether. The solution was cooled to 2°C, followed by dropwise addition of 53 ml of n-butyllithium (1.6M in hexane, 85 mmol). After this had been metered in, the mixture was stirred for half an hour at 2°C and then for 18 hours at room temperature (the lithiumdiphenylphosphine was not completely soluble). Then 100 ml of THF were added, a dark-red homogeneous solution being obtained as a result. This solution was added dropwise to a solution of 19.5 g (85 mmol) of (1,2,3,4-tetramethylcyclopentadien-5-yl)chloromethyldimethylsilane as obtained under a., in 150 ml of THF at 2°C. The reaction mixture was stirred for 18 hours at room temperature, and the THF was then evaporated. 200 ml of petroleum ether were added to the residue, the precipitate was filtered off and the filtrate was boiled down. The residue was pure (diphenylphosphinomethyl) (1,2,3,4-tetramethylcyclopentadien-5-yl)dimethylsilane. The yield was 31.8 g.

c. Synthesis of (1,2,3,4-tetramethylcyclopentadien-5-methyl) (N,N-diisopropylamino)dimethylsilane.

1.22 g of diisopropylamine (12 mmol) was dissolved in 25 ml of THF and cooled to 2°C. Then 7.5 ml of n-butyllithium (1.6 M in hexane; 12 mmol) were added dropwise, followed by half an hour's stirring at room temperature. To the solution obtained, 2.70 g of (1,2,3,4-tetramethyl-cyclopentadien-5-yl)chloromethyldimethylsilane (12 mmol), as obtained under a., were added dropwise. The reaction mixture was stirred at room temperature for 18 hours. The THF was evaporated, and 100 ml of ether were added to the residue, after which the salts formed were filtered off and the filtrate was boiled down, 3.0 g of residue being obtained. GC analysis showed a conversion of 100% and a purity of >90% of (1,2,3,4-tetramethylcyclopentadien-5-methyl) (N,N-diisopropylamino)dimethylsilane.

d. Synthesis of (1,2,3,4-tetramethylcyclopentadien-5-methyl) (N,N-di-n-butylamino)dimethylsilane.

The synthesis under c. was repeated, the starting materials being 1.75 g (13.5 mmol) of di-n-butylamine and 3.05 g of (1,2,3,4-tetramethylcyclopentadien-5-yl)chloromethyldimethylsilane (13.3 mmol). GC analysis showed 100% conversion. After boiling down, 3.95 g of (1,2,3,4-tetramethylcyclopentadien-5-methyl) (N,N-di-n-butylamino)dimethylsilane were obtained.

Example XXXV

Synthesis of 1-(diphenylphosphinoethyl)-2,3,4,5-tetramethylcyclopentadienyltitanium(III) dichloride

$[\text{C}_5\text{Me}_4(\text{CH}_2)_2\text{PPh}_2\text{Ti(III)Cl}_2]$

In a Schlenk vessel, 1.14 g (3.408 mmol) of (diphenylphosphinoethyl)tetramethylcyclopentadiene were dissolved in 30 mL of diethyl ether and the solution was then cooled to -60°C. Then 2.13 mL of n-butyllithium (1.6M in hexane; 3.41 mmol) were added dropwise. The reaction mixture was slowly brought to room temperature, followed by 2 hours stirring. In a second Schlenk vessel 40 mL of tetrahydrofuran were added to 1.26 g of $\text{Ti(III)Cl}_3 \cdot 3\text{THF}$ (3.40 mmol). Both Schlenk vessels were cooled to -60°C and the organolithium compound was then added to the Ti(III)Cl_3 suspension. The reaction mixture was then stirred for 60 hours at room temperature, after which the solvent was evaporated. To the residue 50 mL of petroleum ether were added, which was subsequently evaporated to dryness. There remained a green solid containing 1-(diphenylphosphinoethyl)-2,3,4,5-tetramethylcyclopentadienyltitanium(III) dichloride.

Example XXXXVI1-((dimethylphosphinoethyl)-2,3,4,5-tetramethylcyclopentadienyl)titanium(III) dichloride
[C₅Me₄(CH₂)₂PMe₂Ti(III)Cl₂]

In a Schlenk vessel, 0.78 g (3,709 mmol) of (dimethylphosphinoethyl)tetramethylcyclopentadiene was dissolved in 30 mL of diethyl ether and the solution was then cooled to -60°C. Then 2.32 mL of n-butyllithium (1.6M in hexane; 3.71 mmol) were added dropwise. The reaction mixture was slowly brought to room temperature, followed by 2 hours' stirring. A white suspension was produced.

In a second Schlenk vessel 40 mL of tetrahydrofuran were added to 1.37 g of Ti(III)Cl₃·3THF (3,70 mmol). Both Schlenk vessels were cooled to -60°C and the organolithium compound was then added to the Ti(III)Cl₃ suspension. The reaction mixture was then stirred for 18 hours at room temperature, after which the solvent was evaporated. To the residue 50 mL of petroleum ether were added, which was subsequently evaporated to dryness. There remained a green solid containing 1-((dimethylphosphinoethyl)-2,3,4,5-tetramethylcyclopentadienyl)titanium(III) dichloride.

Example XXXXVIISynthesis of [1-((2-diphenylphosphino-1-sila-1,1-dimethyl)ethyl)-2,3,4,5-tetramethylcyclopentadienyl]titanium(III) dichloride and [1-((2-diphenylphosphino-1-sila-1,1-dimethyl)ethyl)-2,3,4,5-tetramethylcyclopentadienyl]dimethyltitanium(III)
[C₅Me₄(Si(CH₃)₂CH₂)PPh₂Ti(III)Cl₂] and [C₅Me₄(Si(CH₃)₂CH₂)PPh₂Ti(III)Me₂]

To 1.57 g (4.15 mmol) of ((2-diphenylphosphino-1-sila-1,1-dimethyl)ethyl)tetramethylcyclopentadiene, dissolved in 10 mL of diethyl ether, 8.3 mL of lithiumdiisopropylamide (0.5M in diethyl ether; 4.15 mmol) were added at -78°C. After 18 hours' stirring at room temperature, a turbid yellow/orange solution had formed. The diethyl ether was evaporated, and the residue was washed twice with petroleum ether. After this had been well boiled down, there remained 1.41 g of a pale-yellow crystalline product containing lithium ((2-diphenylphosphino-1-sila-1,1-dimethyl)ethyl)tetramethylcyclopentadienyl.

The organolithium compound was dissolved in 20 mL of tetrahydrofuran. Then the yellow/orange solution was added, at -78°C, to 1.36 g (3.76 mmol) of Ti(III)Cl₃·3THF. The reaction mixture was then stirred for 3 hours in the cold bath and afterwards for 18 hours at room temperature. A dark-green solution had now formed, which was boiled down and washed twice with 10mL of petroleum ether. There now remained 1.5 g of a green solid containing 1-((2-diphenylphosphino-1-sila-1,1-dimethyl)ethyl)-2,3,4,5-tetramethylcyclopentadienyl)titanium(III) dichloride.

To 0.534 g (1.08 mmol) of [1-((2-diphenylphosphino-1-sila-1,1-dimethyl)ethyl)-2,3,4,5-tetramethylcyclopentadienyl]titanium(III) dichloride][lithium chloride], 20 mL of diethylether were added, followed by the addition, at -70°C, of 1.35 mL of methylolithium (1.6 M in hexane; 2.16 mmol). After 2 hours' stirring at room temperature, the solvent was removed and the residue dried for 2 hours in vacuo. 20 mL of petroleum ether were then added to the product, followed by filtration. The filtrate was boiled down, followed by drying for 18 hours in vacuo. There remained 0.42 g of a brown/black oil containing [1-((2-diphenylphosphino-1-sila-1,1-dimethyl)ethyl)-2,3,4,5- tetramethylcyclopentadienyl]dimethyltitanium(III).

Example XXXXVIIISynthesis of [1-((2-dimethylphosphino-1-sila-1,1-dimethyl)ethyl)-2,3,4,5-tetramethylcyclopentadienyl]titanium(III) dichloride
[C₅Me₄(Si(CH₃)₂CH₂)PMe₂Ti(III)Cl₂]

To 0.88 g (4.42 mmol) of ((2-dimethylphosphino-1-sila-1,1-dimethyl)ethyl)tetramethylcyclopentadiene, dissolved in 25 mL of diethyl ether, 8.8 mL of lithiumdiisopropylamide (0.5M in diethyl ether; 4.42 mmol) were added at -78°C. After 18 hours' stirring at room temperature, a clear pale-yellow solution had formed. The diethyl ether was evaporated. After this had been well boiled down, there remained 1.14 g of a yellow oil containing lithium ((2-dimethylphosphino-1-sila-1,1-dimethyl)ethyl)tetramethyl-cyclopentadienyl.

The organolithium compound was dissolved in 20 mL of tetrahydrofuran. Then the yellow/orange solution was added, at -78°C, to 1.36 g (3.76 mmol) of Ti(III)Cl₃·3THF. The reaction mixture was then stirred for 3 hours in the cold bath and afterwards for 18 hours at room temperature. A dark-green solution had now formed, which was boiled down and washed twice with 10mL of petroleum ether. There now remained 1.5 g of a green solid containing [1-((2-dimethylphosphino-1-sila-1,1-dimethyl)ethyl)-2,3,4,5-tetramethylcyclopentadienyl]titanium(III) dichloride. 1.13 g (4.41 mmol) of the organolithium compound was dissolved in 30 mL of tetrahydrofuran and cooled to -78°C. This was then added to a cold suspension of 1.67 g (4.5 mmol) of Ti(III)Cl₃·3THF in 25 mL of tetrahydrofuran, followed by 3 hours' stirring at room

temperature. The brown/green slurry was boiled down and washed twice with petroleum ether. Ultimately there remained 730 mg of a dark-green precipitate containing [1-((2-dimethylphosphino-1-sila-1,1-dimethyl)ethyl)-2,3,4,5-tetramethylcyclopentadienyl]titanium(III) dichloride.

5 Example XXXIX

Synthesis of [1-((2-dibutylamino-2-sila-2,2-dimethyl)ethyl)-2,3,4,5-tetramethylcyclopentadienyl]titanium(III) dichloride
[CMe₄(CH₂Si(CH₃)₂)N(n-C₄H₉)₂Ti(III)Cl₂]

10 1.39 g (4.33 mmol) of ((2-dibutylamino-2-sila-2,2-dimethyl)ethyl)tetramethylcyclopentadiene was dissolved in 25 ml of diethyl ether, followed by the addition, at -78°C, of 9.0 mL of lithium dibutylamide (0.5M in diethyl ether; 4.5 mmol). This reaction mixture was stirred for 18 hours, after which a turbid yellow suspension had formed. The solvent was removed, followed by washing with petroleum ether for a number of times. After boiling down completely there remained a yellow/brown oil containing lithium 1-((2-dibutylamino-2-sila-2,2-dimethyl)ethyl)-2,3,4,5-tetramethylcyclopentadienyl.
 15 4.33 mmol of the organolithium compound thus obtained were dissolved in 25 mL of tetrahydrofuran and, at -70°C, added to 1.95 g (5.26 mmol) of Ti(III)Cl₃·3THF in 25 mL of tetrahydrofuran. After 3 hours' stirring at room temperature, the green/brown solution was completely boiled down and washed twice with 10 mL of petroleum ether. There remained 1.5 g of a red/brown oil containing 1-((2-dibutylamino-2-sila-2,2-dimethyl)ethyl)-2,3,4,5-tetramethylcyclopentadienyltitanium(III) dichloride.

20

Polymerization experiments L - LX

A. The copolymerization of ethylene with propylene was carried out in the following manner.

25 A stainless steel reactor of 1 litre was charged, under dry N₂, with 400 mL of pentamethylheptane (PMH) and 30 µmol of triethylaluminium (TEA) or trioctylaluminium (TOA) as a scavenger. The reactor was pressurized to 0.9 MPa with purified monomers and conditioned in such a way that the ratio propylene:ethylene in the gas above the PMH was 1:1. The reactor contents were brought to the desired temperature while being stirred. After conditioning of the reactor, the metal complex (5 µmol) to be used as catalyst component and the cocatalyst (30 µmol of BF₂) were premixed over a period of 1 minute and fed to the reactor by means of a pump. The mixture
 30 was premixed in approximately 25 mL of PMH in a catalyst proportioning vessel and after-rinsing took place with approximately 75 mL of PMH, always under dry N₂ flow.

During the polymerization the monomer concentrations were kept constant as far as possible by supplying the reactor with propylene (125 litres [s.t.p.]/hour) and ethylene (125 litres [s.t.p.]/hour). The reaction was monitored on the basis of the temperature trend and the progress of the monomer feed.

35 After 10 minutes' polymerization the monomer feed was stopped and the solution was drawn off under pressure and collected. The polymer was dried in vacuo for 16 hours at approximately 120°C.

B. The homopolymerization of ethylene and the copolymerization of ethylene with octene were carried out in the following manner.

40 600 mL of an alkane mixture (pentamethylheptane or special boiling point solvent) were introduced as the reaction medium, under dry N₂, into a stainless steel reactor having a volume of 1.5 litres. Then the desired amount of dry octene was introduced into the reactor (this amount can therefore also be zero). The reactor was then, with stirring, heated to the desired temperature under a desired ethylene pressure.

Into a catalyst proportioning vessel having a volume of 100 mL, 25 mL of the alkane mixture were metered in as a solvent. Herein the desired amount of an Al-containing cocatalyst was premixed over a period of 1 minute with the
 45 desired quantity of metal complex, in such a way that the ratio Al/(metal in the complex) in the reaction mixture is equal to 2000.

This mixture was then metered into the reactor, whereupon the polymerization started. The polymerization reaction thus started was carried out isothermally. The ethylene pressure was kept constant at the set pressure. After the desired reaction time the ethylene supply was stopped and the reaction mixture was drawn off and quenched with
 50 methanol.

The reaction mixture containing methanol was washed with water and HCl, in order to remove residues of catalyst. Then the mixture was neutralized with NaHCO₃, after which the organic fraction was admixed with an antioxidant (Irganox 1076, registered trademark) in order to stabilize the polymer. The polymer was dried in vacuo for 24 hours
 at 70°C.

55 In both cases the following conditions were varied:

- metal complex
- type and quantity of scavenger
- type and quantity of cocatalyst

- temperature

The actual conditions are stated in Table I.

Table I

Example	Catalyst complex from Example	Quantity of complex ($\mu\text{mol}/0.5\text{ l}$)	Temperature (°C) and pressure (bar)	Scavenger	Quantity of scavenger (mmol/0.5 l)	Cocatalyst (%)	Ratio Al/M or B/M	Second monomer	Yield (kg/g-M ^{0.5} min)	Comonomer incorporation (m%)	Molecular weight ($\text{Mw} \cdot 10^{-3}$)
L	XXI	5	150 20	TOA	0.2	BF20	2	octene 18 gr.	5	-	-
LI	XVII	5	150 20	TOA	0.2	BF20	2	octene 18 gr.	8	-	-
LII	XVIII	10	150 20	-	-	MAO	1000	-	8	-	-
LIII	XXI	10	120 9	TEA	0.02	BF20	2	propylene ratio 1	16	45.3	23
LIV	XIX	5	150 20	TOA	0.4	BF20	2	-	37	-	-
LV	XXI	10	80 7	-	-	MAO	2000	octene 18 gr.	53	4.7	-

• BF20 : tetrakis(pentafluorophenyl) borate
MAO : methylaluminoxane, from Witco

Claims

- 5 1. Polysubstituted cyclopentadiene-containing compound, of which at least one substituent is of the form $-RDR'_n$, in which R is a linking group between the cyclopentadiene and the group DR'_n , D is a hetero atom selected from group 15 or 16 of the Periodic System of the Elements, R' is a substituent and n is the number of R' groups bound to D, with the exclusion of cyclopentadiene-containing compounds in which:
- 10 - 2 adjacent methyl groups occur at the same time as a substituent in combination with a group of the form $-RDR'_n$, in which R is a methylene group and DR'_n is a dimethylamino group,
- 4 methyl groups occur at the same time as a substituent in combination with a group of the form $-RdR'_n$, in which R is an ethylene or a propylene group and DR'_n is a diphenylphosphinyl group,
- 15 - 4 methyl groups occur at the same time as a substituent in combination with a group of the form $-RdR'_n$, in which R is a dimethylsilylene group and DR'_n is an ethoxy group,
- a tert-butyl group occurs at the same time as a substituent in combination with a group of the form $-RdR'_n$, in which R is an ethylene group and DR'_n is a methoxy group.
- 4 methyl- or ethyl groups occur at the same time as a substituent in combination with a group of the form $-RDR'_n$, in which R is a methylene or ethylene group, D is O, N or S and R' is methyl.
- 20 2. Compound according to Claim 1, in which the R group has the structure
- $$(-ER^3_2)_p$$
- 25 in which $p = 1-4$, E is an element from group 14 of the Periodic System of the Elements, and in which the R^3 groups are each, separately, H or a hydrocarbon radical.
3. Compound according to Claim 1 or 2, in which D is chosen from the group consisting of N, O, P and S.
- 30 4. Compound according to any one of Claims 1-3, in which D is nitrogen.
5. Metal complex comprising a metal from group 4-10 of the Periodic System of the Elements and rare earths in which a compound according to any one of Claims 1 - 4 is present as a ligand.
- 35 6. Metal complex in which the metal is not present in the highest valency state and in which just one polysubstituted cyclopentadiene-containing compound is present as a ligand, of which at least one substituent has the form RDR'_n , in which R is a linking group between the cyclopentadiene and the DR'_n group, D is a hetero atom selected from group 15 or 16 of the Periodic System of the Elements, R' is a substituent and n is the number of R' groups bound to D.
- 40 7. Metal complex according to Claim 6 in which the metal is chosen from the group consisting of Ti, Zr, Hf, V and Cr.
8. Use of a metal complex according to Claim 5-7 as a catalyst component.
- 45 9. Use according to Claim 8 for polymerizing α -olefins.

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which under Rule 45 of the European Patent Convention EP 97 20 1270
shall be considered, for the purposes of subsequent
proceedings, as the European search report

DOCUMENTS CONSIDERED TO BE RELEVANT			
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			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
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INCOMPLETE SEARCH			
<p>The Search Division considers that the present European patent application does not comply with the provisions of the European Patent Convention to such an extent that it is not possible to carry out a meaningful search into the state of the art on the basis of some of the claims.</p> <p>Claims searched completely :</p> <p>Claims searched incompletely :</p> <p>Claims not searched :</p> <p>Reason for the limitation of the search:</p> <p>see sheet C</p>			
Place of search		Date of completion of the search	Examiner
THE HAGUE		29 July 1997	Pauwels, G
CATEGORY OF CITED DOCUMENTS		<p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>Δ : member of the same patent family, corresponding document</p>	
<p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p>			

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INCOMPLETE SEARCH

The Search Division considers that the present European patent application does not comply with the provisions of the European Patent Convention to such an extent that it is not possible to carry out a meaningful search into the state of the art on the basis of some of the claims.

MEANINGFUL SEARCH NOT POSSIBLE ON THE BASIS OF ALL CLAIMS

The cyclopentadiene compounds as defined in the claims can be substituted by a very large group of radicals, which is only limited by the presence of one atom chosen from a relatively limited group. Moreover the structures can be substituted by any other possible group. The claims therefore cover a huge variety of classes of compounds, such that neither a comprehensive search nor a comprehensive search report are possible. The search and the search report are primarily focused on the actually realised subject matter.